

# Effects of Holocene *Alnus* Expansion on Aquatic Productivity, Nitrogen Cycling, and Soil Development in Southwestern Alaska

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## ABSTRACT

Numerous pollen records provide evidence for the widespread range expansion of *Alnus* throughout Alaska and adjacent Canada during the middle Holocene. Because *Alnus* can fix atmospheric N<sub>2</sub>, this vegetational change probably had a profound effect on N availability and cycling. To assess this effect, we analyzed a sediment core from Grandfather Lake in southwestern Alaska for a suite of geochemical indicators, including elemental composition, biogenic silica (BSi) content, and carbon (C) and nitrogen (N) isotopes of organic matter. These data, in conjunction with a pollen record from the same site, are used to infer biogeochemical processes associated with the mid-Holocene *Alnus* expansion. The increase in *Alnus* pollen percentages from 10% to 70% circa 8000–7000 BP (<sup>14</sup>C years before present) suggests the rapid spread of *Alnus* shrub thickets on mountain slopes and riparian zones in the Grandfather Lake region. Coincident with this vegetational change, the mean value of the sediment BSi content increases from 20.4 to 106.2 mg/g, reflecting increased diatom productivity within the lake as a result of *Alnus* N<sub>2</sub> fixation in

the watershed soils and the associated N flux to the lake. Elevated aquatic productivity at this time is also supported by increased percentages of organic C and N, decreased C:N ratios, and decreased values of δ<sup>13</sup>C. Furthermore, the δ<sup>15</sup>N values of sediments increase substantially with the establishment of *Alnus* shrub thickets, suggesting enhanced N availability and accelerated N cycling within the lake and its watershed. Superimposed on a general trend of soil acidification throughout the postglacial period, soil acidity probably increased as a result of the *Alnus* expansion, as can be inferred from decreasing ratios of authigenic base cations to allogenic silica (Si) and increasing ratios of authigenic aluminum (Al) to allogenic Si. The ultimate cause of these mid-Holocene ecosystem changes was an increase in effective moisture in the region.

**Key words:** Holocene paleoecology; biogeochemistry; *Alnus*; nitrogen cycling; aquatic productivity; long-term soil development; nitrogen isotopes; elemental chemistry; lake sediments; Alaska.

## INTRODUCTION

Certain plant types can exert major influences on ecosystem functioning. For example, *Alnus* can in-

crease nitrogen (N) availability and ecosystem productivity because it has the ability to fix atmospheric N<sub>2</sub> through a symbiotic relationship with the *Frankia* actinomycete. Comparisons of forest stands with and without *Alnus* show that its presence significantly increases rates of primary production, carbon (C) accumulation, and N cycling (Bin-

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kley and others 1992; Vogel and Gower 1998). Similarly, soil N increased dramatically when *Alnus* invaded the landscape and decreased when *Picea* replaced *Alnus* as the dominant species during primary succession following glacial recession at the end of the Little Ice Age in Glacial Bay, Alaska (Crocker and Major 1955; Chapin and others 1994). This relationship between plants and ecosystem functions remains valid, despite the fact that the model of vegetational succession described in Crocker and Major (1955) is too simplistic (Fastie 1995). *Alnus* on terrestrial systems can also enhance N availability to the adjacent aquatic systems (Goldman 1961; Engstrom and others 2000). For example, about one-third of the N budget of a Californian lake was derived from leachate of the humus layer that developed beneath *Alnus* trees within the watershed (Goldman 1961). Furthermore, bioassay of the lake water provided evidence that this N input greatly enhanced the productivity of the lake.

Given the prominent effects of *Alnus* on ecosystem N cycling as demonstrated by these modern ecological studies, these effects were probably significant when *Alnus* invaded the landscape in the past. Numerous pollen records from various regions indicate the existence of plant communities with *Alnus* as an important component during the Holocene. In Alaska and adjacent Canada, *Alnus* shrub thickets became established throughout much of the region between 8000 and 7000 BP (Anderson and Brubaker 1994; Cwynar and Spear 1995). This vegetational change was particularly striking in southwestern Alaska, where marked increases in the abundance of *Alnus* pollen provide evidence for the development of the extensive *Alnus* shrub thickets found on mountain slopes and in riparian zones today (Hu and others 1995). How did this mid-Holocene expansion of *Alnus* alter ecosystem functions? Did it increase N availability and accelerate nutrient cycling? Did the productivity of aquatic systems increase as a result of this terrestrial vegetational change? How did the biogeochemical changes associated with the mid-Holocene *Alnus* expansion compare with those documented by comparative and successional studies (Crocker and Major 1955; Goldman 1961; van Cleve and others 1991; Binkley 1992; Engstrom and others 2000)?

To address these questions, we analyzed a sediment core from Grandfather Lake in southwestern Alaska for a suite of elemental and isotopic geochemical indicators. These geochemical analyses offer a means for reconstructing ecosystem processes in relation to past climatic and vegetational changes (Engstrom and Wright 1984; Meyers and Lallier-Verges 1999). For example, the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  val-

ues of lake sediments reflect a number of factors related to C and N cycling, as well as primary productivity within the lake and its watershed (see, for example, Hodell and Schelske 1998; Brenner and others 1999; Talbot and Laerdal 2000). In conjunction with pollen data from the same site (Hu and others 1995), our geochemical results provide new information about biogeochemical processes associated with the mid-Holocene *Alnus* expansion in the region.

## STUDY AREA

Grandfather Lake (50°48'N, 158°31'W, informal name) is an upland lake between the Ahklun Mountains and western Nushagak Lowland (Figure 1). It is morainally dammed and lies within late-Wisconsin glacial limits. The lake has a surface area of 0.35 km<sup>2</sup> and a maximum depth of 20 m. Modern vegetation in the watershed is mixed forest-tundra with dense *Alnus crispa* (green alder) thickets on hillsides and locally abundant stands of *Picea glauca* (white spruce).

The Ahklun Mountains were repeatedly covered by glaciers during the Pleistocene (Briner and Kaufman 2000; Manley and others 2001). Cold and dry periglacial climates during the last glaciation (25,000? to 12,500 BP) are indicated by the Igushik Formation (Lea and others 1991), a widespread eolian sand and loess deposit blanketing the area. Today, the climate is transitional between maritime and continental conditions (NOAA 1980). The mean annual temperature at King Salmon is about +0.7°C, with mean January and July temperatures of -10.3°C and +12.5°C, respectively. Mean annual precipitation in lowland areas ranges from about 45 to 65 cm, with an average of 130–180 cm snow per year. Permafrost is discontinuous in lowlands and absent from uplands (Gallant and others 1995).

Soils are developed in shallow, silty volcanic ash overlying gravelly loam till (Rieger and others 1979; Soil Survey Staff 1999). Typic Humicryods are characteristic of well-drained sites, and Typic Historthels are found on poorly drained soils with permafrost on low foot slopes and valley bottoms. The modern vegetation of the region is characterized by the transition between coastal tundra and interior closed boreal forest (Viereck and others 1992; Gallant and others 1995). Forest communities dominated by *P. glauca* are common on well-drained sites, with dense stands primarily restricted to river bars and lower hillslopes. *Populus balsamifera* (balsam poplar) stands are relatively common on floodplains and south-facing slopes beyond the treeline. Tall shrub thickets of *A. crispa* cover large areas on

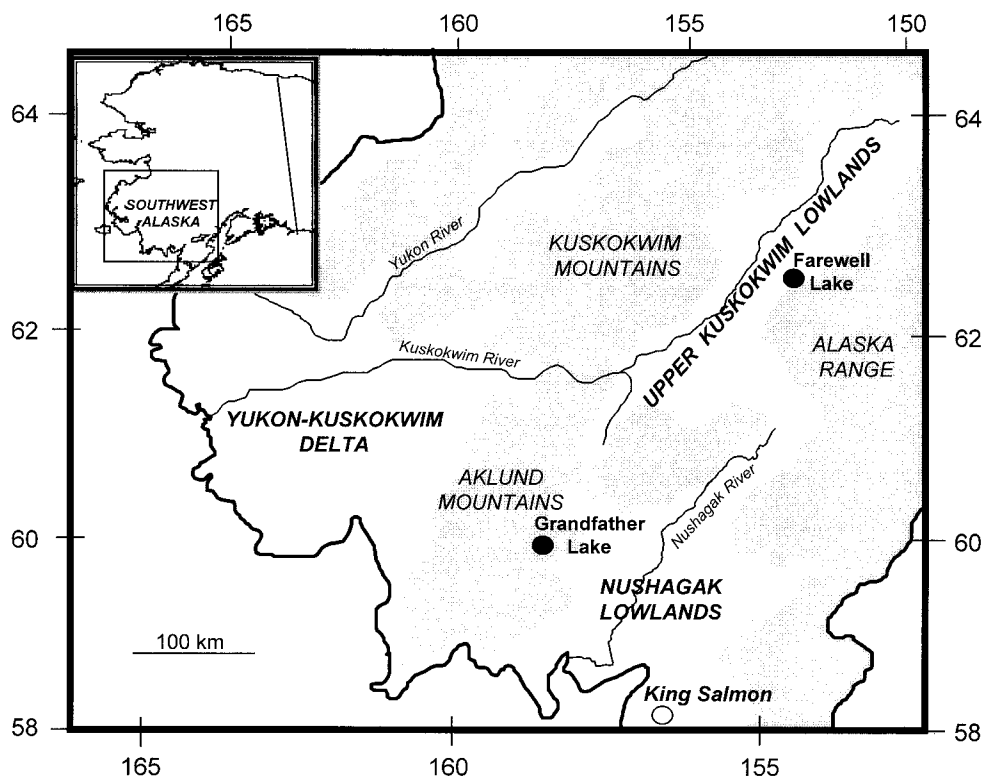


Figure 1. Locations of Grandfather Lake and other sites mentioned in the text.

hillslopes above the altitudinal treeline (300–360 m). Extensive lowland areas are covered by mesic to wet tundra dominated by *Betula glandulosa* (resin birch), *B. nana* (dwarf birch), *Salix* spp. (willows), Cyperaceae (sedge family), Poaceae (grass family), and numerous Ericaceae (heath family) species. Wet meadows with a diverse assemblage of herbaceous taxa and ferns are common on lowlands.

## MATERIALS AND METHODS

Two overlapping sediment cores were recovered from the deepest part (20 m deep) of Grandfather Lake using a modified Livingstone corer (Wright and others 1984). The two cores showed identical lithological features, and they were easily matched with magnetic susceptibility measurement. Sub-samples from one of the cores were taken for pollen analysis and  $^{14}\text{C}$  dating, the methods and results of which have been described in detail elsewhere (Hu and others 1995). The late glacial and early Holocene chronology is problematic at this site (Hu and others 1995), but this does not affect our interpretations of the mid-Holocene ecosystem processes associated with *Alnus* expansion.

The percentages and stable isotopes of C and N in sediments were determined on acid-treated samples

with a Europa 20/20 mass spectrometer at the University of Alaska. Isotopic results were reported in  $\delta$  notation ( $\delta = ([R \text{ sample}/R \text{ standard}] - 1) \cdot 1000$ , where  $R = {}^{13}\text{C}/{}^{12}\text{C}$  or  ${}^{15}\text{N}/{}^{14}\text{N}$ ). Analytical precision was better than  $\pm 0.1\text{‰}$  for bulk organic  $\delta^{13}\text{C}$  and  $\pm 0.3\text{‰}$  for bulk organic  $\delta^{15}\text{N}$  on laboratory standards and on duplicate samples. All isotope results were expressed relative to the international standards: Vienna Peedee Belemnite (VPDB) for  $\delta^{13}\text{C}$  and atmospheric  $\text{N}_2$  (AIR) for  $\delta^{15}\text{N}$ .

Sediment preparation for the analysis of other elements follows Engstrom and Wright (1984) with some modifications. Fraction 1, the authigenic fraction, was obtained by filtering the sample through a  $0.45\text{-}\mu\text{m}$  Millipore filter after oxidation with 30% hydrogen peroxide and extraction with hot 0.3 M HCl. This fraction is deposited directly from aquatic solution through biological uptake or chemical sorption and precipitation. It includes biochemically precipitated carbonate minerals, oxyhydroxides and organic chelates of iron (Fe) and manganese (Mn), sulfides, phosphates, and sorbed or coprecipitated elements. Fraction 2, the allogenic fraction for all elements other than silica (Si), was prepared by the complete fusion of the remaining clastic residue (rock fragments) in lithium metaborate, followed by dissolution of the molten bead in 0.5 M HCl. This

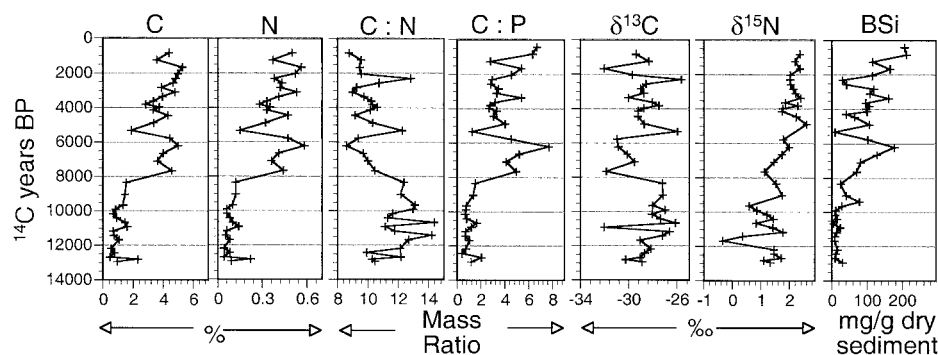


Figure 2. Percentages and stable isotope ratios of carbon (C) and nitrogen (N), mass ratios of C to N and C to phosphorus (P) (P in authigenic fraction), and concentrations of biogenic silica (BSi) in the sediments of Grandfather Lake.

fraction includes all minerals deriving from outside the lake proper through catchment soil erosion or eolian activity. Elemental composition of these two fractions was determined by inductively coupled argon plasma/atomic emission spectroscopy (Thermo Jarrel Ash ICAP61E). Allogenic Si was determined by subtracting the amount of biogenic silica (BSi) from that of Si in fraction 2. BSi, a chemical measure of the abundance of diatom remains in sediments, was extracted from a separate sample using 2M  $\text{Na}_2\text{CO}_3$  and determined with a spectrophotometer (Perkin-Elmer 55E) following the procedure described by Mortlock and Froelich (1989).

## RESULTS

Carbon and nitrogen in the Grandfather Lake sediments range from 0.5% to 5.3% and 0.04% to 0.6% of dry sediments, respectively (Figure 2). All measured N is associated with organic matter, as suggested by the negative N% intercept of a linear model relating N% and C% ( $\text{N}\% = -0.029 + 0.110 \bullet \text{C}\%$ ) (Figure 3). Both C% and N% show a marked increase circa 8000 BP, and their stratigraphic variations are significantly correlated (Figure 3). The mass ratios of C to N, which have a range of 8.6 to 14.3, are generally lower after circa 8000 BP than before that time. BSi content is consistently low (8.2–30.1 mg/g dry sediment) at 12,500–10,000 BP and intermediate (10.7–77.8 mg/g dry sediment) at 10,000–8000 BP (Figure 2). BSi increases to 126.9 mg/g dry sediments between 8000 and 6500 BP and remains generally high, with some fluctuations, thereafter. The mean value of BSi is 20.4 and 106.2 mg/g dry sediments before and after 8000 BP, respectively.

The values of  $\delta^{13}\text{C}$  for the sediments of Grandfather Lake are relatively high ( $-33.0\text{‰}$  to  $-26.0\text{‰}$ ), with an increasing trend from 12,500 to 8000 BP (Figure 2).  $\delta^{13}\text{C}$  then decreases steadily to  $-32.0\text{‰}$

at 6000 BP and fluctuates around  $-29.0\text{‰}$  thereafter.  $\delta^{13}\text{C}$  is correlated negatively with BSi and positively with C:N ratio (Figure 3).  $\delta^{15}\text{N}$  fluctuates around  $1.0\text{‰}$  without major stratigraphic trends before 8000 BP. It then increases steadily by  $1.5\text{‰}$  between 8000 and 5000 BP and remains consistently high ( $1.9\text{‰}$  to  $2.3\text{‰}$ ) thereafter.  $\delta^{15}\text{N}$  is negatively correlated with C:N and not significantly correlated with  $\delta^{13}\text{C}$ .

The concentrations of a suite of eight elements (Figure 4) were measured in the two separate fractions described in the Methods section. Within the authigenic fraction, the order of stratigraphically averaged abundance for the elements analyzed is:  $\text{Fe} > \text{Al} > \text{Si} > \text{Ca} = \text{Mg} > \text{Na} > \text{Mn} > \text{Ba}$ . This abundance order suggests that the organic chelates and oxyhydroxides of iron and aluminum are dominant components of the authigenic fraction. Several elements (Mn, Mg, Ba) show a slight decrease over time, whereas Al shows a slight increase. In addition, the ratio of Fe to Mn, a commonly used proxy indicator for the redox state of watershed soils or within the lake, shows a steady increase after 4000 BP (Figure 5). Within the allogenic fraction, the order of stratigraphically averaged abundance is:  $\text{Si} > \text{Al} > \text{Na} > \text{Fe} > \text{Ca} > \text{Mg} > \text{Ba} > \text{Mn}$ . This abundance sequence suggests that the allogenic fraction is dominated by aluminum silicates. The concentrations of most of these elements are relatively high before 10,000 BP, after which they show a decreasing trend.

## DISCUSSION

Each of the geochemical indicators used in this study is determined by a number of environmental and diagenetic factors. As a result, our ecosystem interpretations based on the geochemical data from Grandfather Lake are somewhat speculative. In addition, most of our geochemical records exhibit large stratigraphic variations throughout the post-

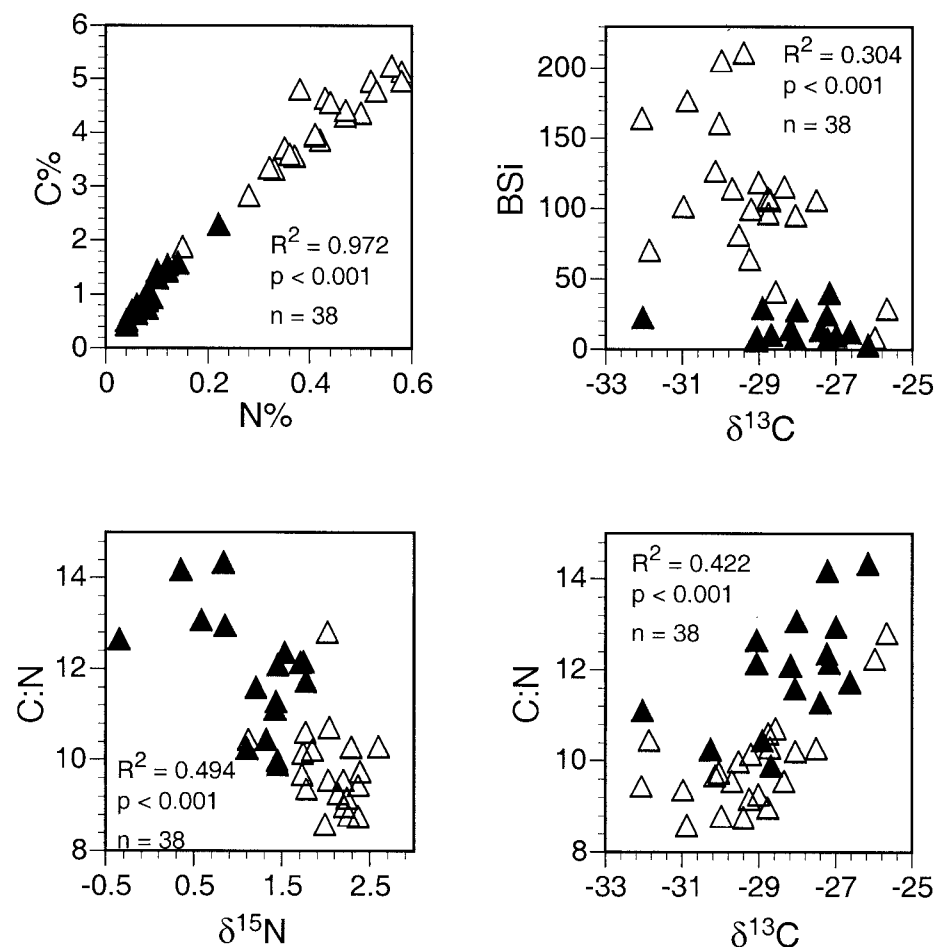


Figure 3. Statistical relationships between various geochemical indicators in the sediments of Grandfather Lake. Solid triangles represent samples earlier than 8000 BP (before *Alnus* expansion); empty triangles represent samples later 8000 BP (after *Alnus* expansion).

glacial period (Figures 2, 4, and 5). Some of these variations are unrelated to terrestrial vegetational changes as inferred from our pollen data (Figure 6). Nevertheless, there are coherent patterns among various geochemical proxies that suggest major changes in ecosystem processes corresponding to the mid-Holocene establishment of *Alnus* shrub thickets. Here we focus our discussion on the effects of the mid-Holocene *Alnus* expansion on aquatic productivity, N cycling, and soil development at Grandfather Lake.

#### Increased Aquatic Productivity in Response to *Alnus* Expansion

The low but continuous appearance of *Alnus* pollen at 9000–8000 BP (Figure 6) represents small local populations of *Alnus* shrubs or long-distance pollen transport. The dramatic increase in *Alnus* pollen percentages circa 8000–7000 BP indicates the rapid spread of *Alnus* shrub thickets on mountain slopes and along riparian zones in the region (Hu and others 1995). *Alnus* pollen percentages and accu-

mulation rates in southwestern Alaska are unusually high compared to those in the pollen records from other areas of Alaska, apparently reflecting the extremely high density of *Alnus* shrub thickets that characterize the region today.

Marked changes in BSi, C:N, and  $\delta^{13}\text{C}$  together suggest increased aquatic productivity and accelerated nutrient cycling at Grandfather Lake circa 8000 BP, coinciding with the establishment of *Alnus* shrub thickets. In particular, the content of BSi is substantially higher after *Alnus* expansion than before, despite its large variations throughout the profile. Sedimentary BSi content reflects the abundance of the remains of diatoms (Conley 1988), which are commonly dominant primary producers in temperate and boreal lakes (Wetzel 1983). Thus, the marked increase in BSi between 8000 and 6500 BP suggests that diatoms became more abundant and that the primary productivity of Grandfather Lake increased with the expansion of *Alnus* within the watershed. This increase of BSi content is not caused by decreased mineral matter related to soil

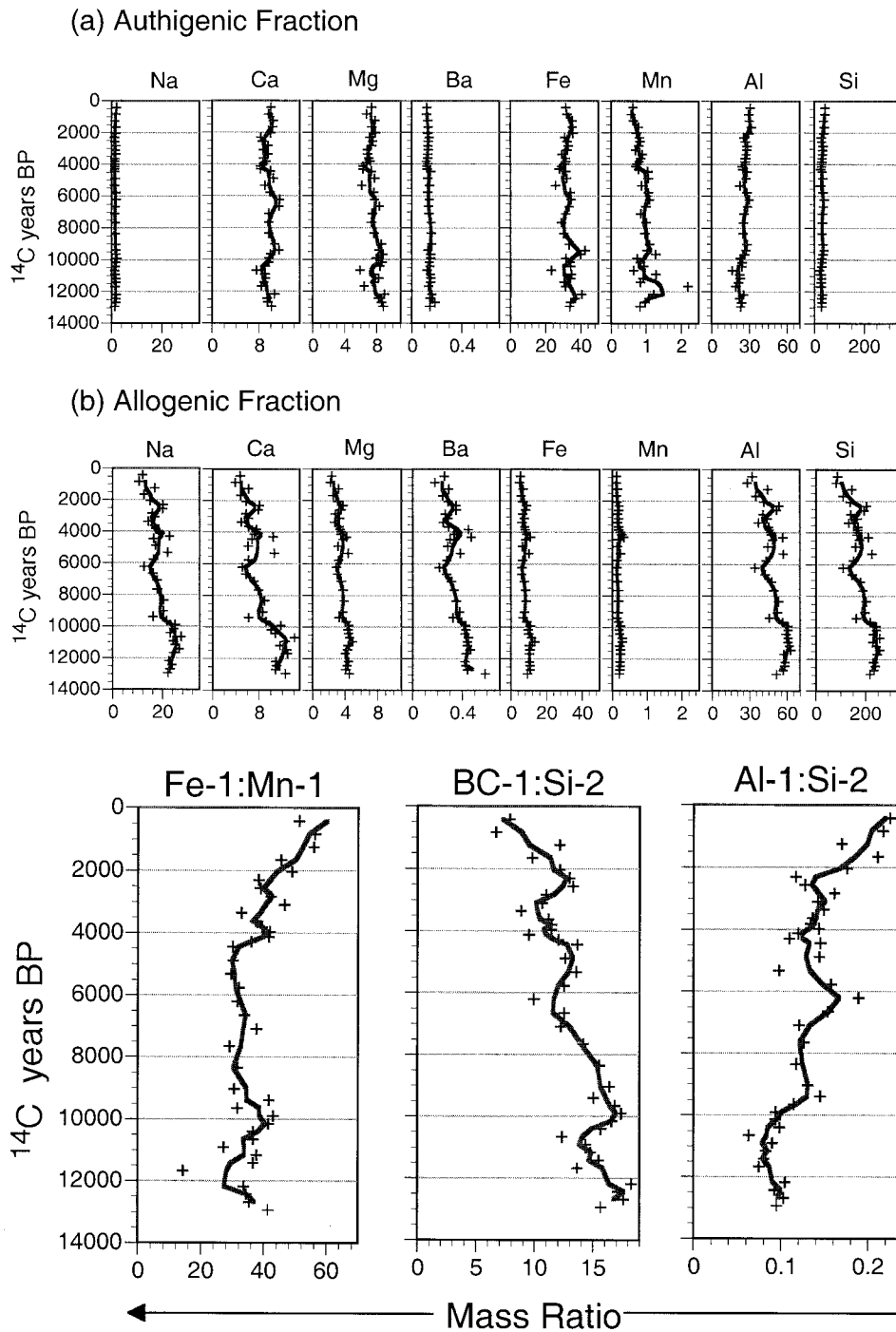


Figure 4. Elemental composition in the (a) authigenic and (b) allogenic fractions of the sediments from Grandfather Lake. Unit for all elements: mg/g dry sediments. Crosses represent original data; curves are based on three-point running averages.

Figure 5. Mass ratios of Fe to Mn in the authigenic fraction, the sum of three base cations (BC = Na + Ca + Mg) in the authigenic fraction to Si in the allogenic fraction, and Al in the authigenic fraction to Si in the allogenic fraction. 1 = authigenic fraction; 2 = allogenic fraction. Crosses represent original data; curves are based on three-point running averages.

stabilization. The ratio of BSi to organic matter is independent of sedimentary mineral content, and it probably reflects aquatic productivity relative to terrestrial productivity. This ratio is also generally higher after circa 8000 BP than before, suggesting increased aquatic productivity at 8000 BP.

Consistent with BSi, the percentages of organic C and N both increase greatly, probably as a result of

the increased production of aquatic organic matter enriched in N. An increase in aquatic productivity is further supported by lower C:N ratios after the *Alnus* expansion than before. The range of C:N values is typically lower for aquatic organic matter than for terrestrial organic matter (Meyers and Lallier-Verges 1999). C:N ratios are 6.0–9.0 for planktonic organisms and 20.0–100.0 for terrestrial plant tis-

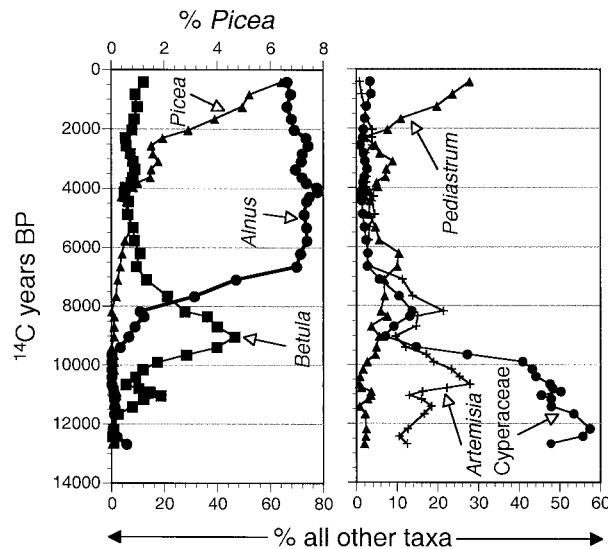


Figure 6. Pollen percentages of key taxa (*Alnus*, *Picea*, *Betula*, *Artemisia*, *Pediastrum*, and *Cyperaceae*) at Grandfather Lake. Three-point averages of the original data are plotted to highlight major trends. For a complete pollen diagram, see Hu and others (1995).

sue, soil, and peat (see, for example, Brenner and others 1978; Meyers 1994; Tyson 1995). There are some exceptions to these C:N ranges. For example, soils under  $N_2$ -fixing *Alnus* have C:N values of approximately 17.0 (Hobbie and others 2000), and algal C:N values of more than 14.6 can be achieved where N supplies are severely limited (Hecky and others 1993). The range of C:N ratio (8.7–14.3) for the Grandfather Lake sediments represents a mixture of aquatic and terrestrial organic matter in various proportions. The marked decrease in C:N ratio following *Alnus* establishment suggests an increase in the proportion of aquatic organic matter resulting from increased aquatic productivity. In addition, the input of terrestrial organic matter enriched in N as a result of *Alnus* establishment may have contributed to this sedimentary C:N decrease.

Changes in aquatic productivity can also be inferred from sedimentary  $\delta^{13}C$  values (see, for example, Gu and others 1996; Hodell and Schelske 1998; Brenner and others 1999; Meyers and Lallier-Verges 1999). The  $\delta^{13}C$  values of bulk lake sediment organic matter are determined by the relative abundance of aquatic vs terrestrial organic matter, among a number of other factors (McKenzie 1985; Meyers and Lallier-Verges 1999). Previous studies have shown that the  $\delta^{13}C$  ranges overlap for lake algae and  $C_3$  land plants (for a recent review, see Meyers and Lallier-Verges 1999). However, Kling and others (1992a) found that algae are more de-

pleted in  $^{13}C$  than terrestrial organic matter in some Alaskan lakes. If we assume that their results are applicable to Grandfather Lake, the mid-Holocene  $\delta^{13}C$  decrease indicates increased aquatic productivity and thus enhanced contribution of algae-derived C to the sedimentary C pool. This interpretation is supported by the positive correlation between  $\delta^{13}C$  and C:N and the negative correlation between  $\delta^{13}C$  and BSi (Figure 3); these three proxies consistently suggest increased aquatic productivity at Grandfather Lake during the mid-Holocene.

The increase in the productivity of Grandfather Lake circa 8000 BP coincides with the widespread *Alnus* expansion in the region.  $N_2$  fixation by *Alnus* within the watershed increased N fluxes to the lake, thereby relaxing N limitation and stimulating diatom productivity. Such an interpretation is consistent with a marked increase in the  $\delta^{15}N$  values of the lake sediments at the time of *Alnus* expansion. Elevated aquatic productivity in response to *Alnus*  $N_2$  fixation at Grandfather Lake circa 8000 BP implies that the lake was N-limited during the early Holocene.

However, phosphorus (P) availability is also known to be a major factor curtailing the primary productivity of many modern lakes (Horne and Goldman 1994). For example, Elser and others (1990) reviewed the results of nutrient-limitation experiments at a number of North American lakes and concluded that the addition of N or P alone both increased productivity. The magnitudes of productivity increases were much greater when both N and P were added, suggesting colimitation by N and P. Similar results of N and P colimitation have been reported from field experiments in the Toolik Lake area on the North Slope of Alaska (Kling and others 1992b).

Could enhanced P availability contribute to the increase in aquatic productivity at Grandfather Lake circa 8000 BP? In contrast to C:N ratios, the ratios of C:P increase at the time of the *Alnus* expansion, indicating decreased P relative to C; this may have been caused by enhanced P recycling for primary production due to the increased availability of N. This interpretation is supported by the overall opposite stratigraphic variations in C:N and C:P ratios after 8000 BP. The decrease in C:P probably resulted from soil stabilization and decreased eolian activity with the widespread establishment of *Alnus* through Alaska and adjacent Canada, because P sources for many lakes are primarily watershed bedrock and eolian dust (Horne and Goldman 1994).

There are numerous pollen records documenting the mid-Holocene spread of *Alnus* in Alaska and

adjacent Canada (Anderson and Brubaker 1994; Cwynar and Spear 1995). Little information, however, is available about the history of aquatic productivity to verify our results from Grandfather Lake. Nevertheless, fossil diatom analysis of a sediment core from Birch Lake in interior Alaska (Gregory-Eaves 1998) shows that coinciding with *Alnus* expansion, oligotrophic assemblages changed to mesotrophic assemblages. This change is consistent with the interpretation of the N fertilization effect of *Alnus* on aquatic systems.

### Increased Availability and Accelerated Cycling of Nitrogen

Ecosystems with high rates of N cycling tend to have high  $\delta^{15}\text{N}$  values (Nadelhoffer and Fry 1994; Gu and others 1996; Talbot and Laerdal 2000). The increase in  $\delta^{15}\text{N}$  at Grandfather Lake beginning at about 8000 BP thus suggests accelerated N cycling, probably within both the terrestrial and aquatic constituents of the system. The steady increase in  $\delta^{15}\text{N}$  from 8000 to 5000 BP reflects a gradual increase in the overall rate of N cycling during this period to reach a state similar to that of the present by 5000 BP.  $\text{N}_2$  fixation by *Alnus* resulted in increased pool sizes of ammonium and nitrate, such that fractionations during transformations of these compounds were not substrate-limited and became more pronounced. The residual N pools in vegetation and soils then became enriched in  $^{15}\text{N}$  as more highly fractionated,  $^{15}\text{N}$ -depleted compounds were lost. Increases in soil N turnover and mineralization rates also increased the relative amount of plant-available N supplied from the mineralization of older, more decomposed humus, which is generally rich in  $^{15}\text{N}$ .

If the N pool within the watershed of Grandfather Lake was rich in  $^{15}\text{N}$ , the N supply from the watershed to the lake through groundwater and surface runoff would become  $^{15}\text{N}$ -enriched. The uptake of this N by aquatic organisms thus resulted in  $^{15}\text{N}$ -enriched aquatic organic matter. In addition, the length of the food chain within an aquatic system is known to increase with increased primary productivity (Kaunzinger and Morin 1998). This process probably occurred at Grandfather Lake circa 8000 BP. Because a 3‰–4‰ increase in  $\delta^{15}\text{N}$  occurs for each trophic level in the food web (Minagawa and Wada 1984; Peterson and Fry 1987), such a change in the trophic structure of the lake should have led to an overall  $^{15}\text{N}$  enrichment of aquatic organic matter. Thus, changes in the N processes within the lake itself probably contributed to the marked increase in  $\delta^{15}\text{N}$  at 8000–5000 BP.

Alternative interpretations exist for the marked

increase in  $\delta^{15}\text{N}$  at 8000–5000 BP. In particular, the  $\delta^{15}\text{N}$  values of terrestrial organic matter incorporated into the sediments may differ before and after *Alnus* expansion. However, throughout the Grandfather Lake record, no stratigraphic trend in  $\delta^{15}\text{N}$  can be explained by pollen-inferred vegetational change (Figures 2 and 6) and the tissue  $\delta^{15}\text{N}$  values of end-member plant taxa (Nadelhoffer and others 1996). For example, Cyperaceae plants have higher  $\delta^{15}\text{N}$  values than *Alnus crispa*, both of which have much higher  $\delta^{15}\text{N}$  values than *Betula nana*. However, our sediment  $\delta^{15}\text{N}$  data do not indicate higher values during the early postglacial period, when Cyperaceae dominated the herb tundra, than during the middle and late Holocene, when *Alnus* shrub thickets prevailed over the landscape (Figures 2 and 6). Similarly,  $\delta^{15}\text{N}$  values were not particularly low during the period circa 9000 BP, when *Betula* shrub tundra was the dominant vegetation type.

Another possible cause for increased  $\delta^{15}\text{N}$  is a change from oxic to anoxic conditions in the hypolimnion of the lake. Denitrification in suboxic waters has been invoked to explain  $\delta^{15}\text{N}$  variations related to glacial–interglacial climatic cycles in oceans (Ganeshram and others 1995). If a change from an oxic to suboxic hypolimnion at Grandfather Lake occurred around 8000 BP, enhanced denitrification could lead to a  $^{15}\text{N}$ -enriched N pool. Such a change in hypolimnetic redox conditions could have resulted in the loss of redox-sensitive elements, such as Fe and Mn. No changes in Fe and Mn concentrations or Fe:Mn ratios occurred at this time in our elemental record (Figures 4 and 5), suggesting that the hypolimnion of Grandfather Lake did not become anoxic. However, denitrification occurs at higher redox potentials than Mn and Fe reduction; thus, the lack of Fe and Mn evidence for hypolimnetic anoxia does not negate denitrification as a cause of the  $\delta^{15}\text{N}$  increase at 8000–5000 BP at Grandfather Lake.

### Soil Development in Relation to Vegetational Change

High allogenic concentrations of all elements at 12,500–10,000 BP reflect unstable soils (Engstrom and Wright 1984) as a result of frequent solifluction events on the early postglacial landscape. Such soil conditions are consistent with pollen data indicating herb tundra with sparse vegetational cover within the watershed during this period (Hu and others 1995). The decreases in the allogenic concentrations of most elements around 10,000 BP suggest decreased soil erosion and reduced influx of mineral matter from the watershed to the lake.

These changes resulted from the widespread invasion of *Betula* shrubs throughout the herb tundra due to climatic warming at the end of the Younger Dryas (Hu and others 1995). The allogenic concentrations of most elements continue to decline from 10,000 to 6000 BP, suggesting further soil stabilization with the continual expansion of vegetational cover.

The establishment of *Alnus*-dominated vegetation can induce soil acidification (Crocker and Major 1955; Binkley and others 1992), as soil acidity increases with elevated concentrations of nitrate and organic acids. For example, soil pH decreased markedly during the *Alnus*-dominated successional stage (Crocker and Major 1955). Similarly, the mid-Holocene *Alnus* expansion may have increased soil acidity at Grandfather Lake, as suggested by the generally lower ratios of total base cations within the authigenic fraction to allogenic Si ([BC-1:Si-2] ratio) and higher ratios of authigenic Al to allogenic Si ([Al-1:Si-2] ratio) after *Alnus* expansion than before (Figure 5).

A number of previous studies have shown that natural and anthropogenic soil acidification tends to result in the depletion of base cation pools followed by the increase of extractable Al (see, for example, Mulder and Stein 1994; Likens and others 1996). Such processes probably occurred in the soils of the Grandfather Lake watershed at the time of *Alnus* expansion. When the leached elements from the watershed soils entered the lake through groundwater, the base cations would be lost via the lake outlet, because these elements are highly mobile. The drainage of nitrate and organic acids from the watershed to the lake as a result of *Alnus* expansion provided an additional mechanism for the loss of base cations from the lake. In contrast, Al formed organic chelates and oxyhydroxides, which eventually settled to the bottom of the lake and became incorporated into the sediments. These processes would have resulted in decreased (BC-1:Si-2) ratios and increased (Al-1:Si-2) ratios in the sediments of Grandfather Lake.

Soil acidification, however, occurred throughout the postglacial history within the watershed of the lake, as suggested by the more or less continuous decreases in the (BC-1:Si-2) ratio and increases in the (Al-1:Si-2) ratio from 12,000 BP to the present. For example, although (BC-1:Si-2) ratios are generally lower and (Al-1:Si-2) ratios are higher after the *Alnus* expansion, the magnitudes of the changes in these ratios are comparable or greater during the last 2000 years. The soils of the Grandfather Lake watershed became progressively more acidic as a result of gradual accumulation of soil organic mat-

ter and the consequent increase in organic acids. Coniferous litterfall favors such processes (see, for example, Cronan and Aiken 1985; Chapin and others 1994), which became intensified during the last 2000 years when the populations of *Picea* expanded in the region (Hu and others 1995).

In addition to acidification, soil redox chemistry at Grandfather Lake changed substantially in the past 4000 BP, as suggested by a steady increase in the Fe:Mn ratio within the authigenic fraction. Because Fe requires lower redox values than Mn to be released from soils, an increase in the Fe:Mn ratio of lake sediments has been used to infer changes from oxic to suboxic conditions in watershed soils (Mackereth 1966; Engstrom and Wright 1984; Hu and others 1996). For example, on the basis of a pronounced increase in the authigenic Fe:Mn ratio of sediments from Farewell Lake on the northern foothills of the Alaska Range, we suggested in an earlier study (Hu and others 1996) that the watershed soils of this lake became waterlogged at 4000 BP, probably induced by a rise in the permafrost table due to climatic cooling. These processes led to the development of extensive peatlands and modern boreal forests dominated by *Picea mariana* in the Farewell Lake region. Similar processes occurred at Grandfather Lake, as can be inferred from the increasing Fe:Mn ratios beginning at 4000 BP. These edaphic alterations occurred in lowland areas where extensive treeless wetlands exist today; the upland sites occupied by *Picea glauca* trees remained well drained. Concurrent soil changes at Grandfather and Farewell lakes, which are approximately 300 km apart, imply that these changes were driven by a regional climatic change (Hu and others 1998).

## CONCLUSIONS

The effects of *Alnus* on ecosystem functions have been well documented through comparative (that is, forests with and without *Alnus*) and successional studies (Crocker and Major 1955; van Cleve and others 1991; Binkley and others 1992). These studies show that *Alnus* N<sub>2</sub> fixation can greatly enhance primary productivity and N cycling. Our results from Grandfather Lake are broadly consistent with the results of these studies and illustrate that similar processes played an important role in ecosystem dynamics at much longer time scales. Specifically, the establishment of *Alnus* shrub thickets within the Grandfather Lake watershed resulted in increased aquatic productivity, accelerated N cycling, and probably soil acidification. The ultimate cause for these ecosystem changes at Grandfather Lake circa 8000 BP was a climatic change. Recent limno-geo-

chemical and lake-level studies in Alaska (Hu and others 1998; Abbott and others 2000) have provided evidence for an increase in effective moisture in the region at this time. The fact that *Alnus* spread more or less simultaneously throughout the vast region of Alaska and adjacent Canada at this time also implies that this vegetational change was driven by climatic factors (Anderson and Brubaker 1994; Cwynar and Spear 1995). As our results from Grandfather Lake demonstrate, this widespread vegetational change probably exerted profound influences on ecosystem productivity and nutrient cycling throughout the region.

Paleoecological analyses provide a powerful tool for understanding patterns of long-term ecological changes. However, biogeochemical processes associated with vegetational changes are difficult to decipher from conventional paleo-records from lake sediments, such as pollen data. Geochemical analyses of lake sediments offer a means to infer ecosystem processes in relation to past climatic and vegetational changes. These inferences are often ambiguous because each geochemical indicator in sediments is determined by a number of environmental and diagenetic factors. However, coherent interpretations can be derived by simultaneously applying several proxy indicators that provide constraints for one another. For example, it is often difficult to separate terrestrial and aquatic signals of C isotopic changes, but changes in BSi, C:N, and  $\delta^{13}\text{C}$  together offer strong evidence for increased aquatic productivity circa 8000 BP at Grandfather Lake. This study demonstrates that despite the difficulties in disentangling the numerous controls of geochemical variation in lake sediments (Engstrom and Wright 1984; Meyers and Lallier-Verges 1999), such records can help to elucidate ecosystem processes. This approach provides information on the temporal variation of biogeochemical cycling complementary to that based on space-for-time substitution (see, for example, Chadwick and others 1999).

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