These kinetic results portray a distinct pattern of the order-disorder relationship in anthophyllite as compared with other chain silicates: The temperature dependence of the rate constants is much greater (the activation energy for disordering in orthopyroxenes is ~20 kcal/formula unit), and, although both rate constants must decrease with decreasing temperature, the rate constant for disordering must decrease more than that for ordering. The temperature dependence of the rate constants therefore explains the data at 550°C, which show that equilibrium is not attained by disordering within the time scale for equilibrium ordering. Likewise it follows that a disordering experiment at 400°C for 907 hours does not show any change in the $Fe^{2+}$-Mg distribution. In fact, a change in $X^{Fe}_{M4}$ of 0.001 at this temperature would require a run duration of some 4 years. From these kinetic results, there is no evidence for a high-temperature thermal barrier as previously anticipated, and the degree of ordering in the natural anthophyllite can be quantitatively interpreted in terms of the measured rate constants. Of course, at very low temperatures the ordering process will be terminated owing to slow reaction kinetics after $\sim 10^7$ years.

From the rate constants the $X^{Fe}_{M4}$ values that are attained after a given time interval at a given temperature can be calculated, provided that the $X^{Fe}_{M4}$ of the starting material is known. Figure 1 shows such a time-temperature-percentage transformation diagram plotted on a logarithmic time scale and also includes a model cooling history of a rock in terms of temperature and time. From a variety of possible cooling paths for this rock a linear cooling rate of $2.5 \times 10^{-5}$°C year$^{-1}$ is shown, estimated from the closing temperatures of muscovite and biotite and their apparent Rb-Sr age difference (for example, see *15*). From this diagram it might be concluded that the anthophyllite orders completely down to some 260°C and attains an $X^{Fe}_{M4}$ value of 0.537 after $\sim 10^7$ years. The inferred cooling history for anthophyllite refers of course to a rapid quench from the crystallization temperature (taken as close to the upper stability limit for anthophyllite, ~720°C in Fig. 1) to the temperature under consideration. In this model the cooling path of the rock is significantly longer than the equilibrium ordering path for anthophyllite, as can be seen in Fig. 1 from the minimum times for equilibrium at successively lower temperatures.

However, the minimum ordering temperature will be different from that deduced from Fig. 1 for different crystallization temperatures. For example, if complete intracrystalline equilibrium is assumed at 300°C and the rock is then cooled with the same linear temperature-time gradient as above (Fig. 2), the lowest $X^{Fe}_{M4}$ value that might be attained is between ~0.531 and 0.532 at 268°C, indicating an apparent equilibration temperature $T_{ae}$ of 277°C. Thus, in the temperature range of interest a nearly equilibrated crystal orders more slowly than an unequilibrated phase, and the limiting $X^{Fe}_{M4}$ values derived from these two specific rock-cooling models represent maximum or minimum apparent equilibration temperatures, respectively. Of course, in a model where the sample is held at the crystallization temperature and then quenched to room temperature, the crystallization temperatures would themselves be the apparent equilibration temperatures.

Table 2. Disordering rate constants, $k_{4\text{-}123}$, where $K^\circ_{123\text{-}4} = k_{123\text{-}4}/k_{4\text{-}123}$, determined for the natural anthophyllite at 500° and 550°C and calculated activation energies for disordering, $E_{aD}$.

| Experiments | $k_{4\text{-}123}$ (year$^{-1}$) | | $E_{aD}$ (kcal) |
|---|---|---|---|
| | 550°C | 500°C | |
| Ordering | 37.8432 | 3.3112 | 61.6 |
| Disordering | 5.0458 | 0.57816 | 54.8 |

From models similar to those inferred in Figs. 1 and 2 but with different initial $X^{Fe}_{M4}$ values corresponding to different crystallization temperatures $T_s$, it can be shown that the rate constants of the exchange process together with the $X^{Fe}_{M4}$ of the natural crystal impose limits on the rate of cooling of the rock. In Fig. 3 the apparent minimum equilibration temperatures have been evaluated for three different temperature-time gradients and are plotted as a function of the crystallization temperature. For a given cooling rate, all values of $T_s$ between $T_{ae} = T_s$ and the apparent equilibration temperature in the natural sample would be permissible. The observed $T_{ae}$ of 270°C in the Rabbitt anthophyllite thus indicates a *maximum* linear cooling rate of $\sim 1 \times 10^{-4}$ °C year$^{-1}$ for all values of $T_s$ within the anticipated stability field for this particular composition. This value might be subject to an error of about one order of magnitude, however, because it depends on the uncertainty of the $T_{ae}$ value and thus on the invariancy of the $\Delta G^\circ_{ex}$ with temperature.

In conclusion, the kinetic results presented here imply that the measured $T_{ae}$ values in natural anthophyllites directly reflect the cooling rate of rock system. Furthermore, it can be inferred that the time-temperature-percentage transformation plots of coexisting chain silicates will ultimately define the specific rock-cooling path during the later stages of the cooling history.

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## Forest Fire: Effects on Phosphorus Movement to Lakes

Abstract. *After a wildfire in the virgin forest of a lake-watershed region in northeastern Minnesota, the phosphorus concentration in the runoff was elevated for 2 years and decreased in the third year. However, there was no increase in the phosphorus concentrations of a lake and its input stream. This indicates that, under similar circumstances, controlled burning will not damage streams or lakes by elevating phosphorus levels.*

Does fire in a forested watershed release sufficient nutrients to stimulate eutrophication of streams and lakes? This question needs to be answered because new forest management policies are being introduced which would allow wildfires to burn in wilderness areas and would use fire as a tool to maintain natural species compositions (*1*). These policies indicate recognition that many existing forests are products of wildfires (*2*). The popular message of "Smokey Bear," that fire destroys for-

Table 1. Percentage changes in water volume and quantity of phosphorus during the snow-free season in throughfall, overland flow, and soil water at the burned watershed of Meander Lake, relative to amounts at the unburned watershed of Dogfish Lake, after the Little Sioux wildfire in northeastern Minnesota, 14 to 17 May 1971.

| Year | Throughfall | | Overland flow | | Soil water | |
|---|---|---|---|---|---|---|
| | Volume (%) | Phosphorus (%) | Volume (%) | Phosphorus (%) | Volume (%) | Phosphorus (%) |
| 1971 | - 8 | -17 | +28 | +392 | +21 | +47 |
| 1972 | +14 | -26 | +98 | + 52 | + 8 | +68 |
| 1973 | + 9 | -28 | +41 | - 59 | + 2 | -34 |

ests, has been challenged (*3*), and fire has been reconsidered as a natural and necessary component of many forest ecosystems (*2*).

This report documents the effects of a wildfire in a Minnesota forest on phosphorus movement to streams and lakes from watersheds in that forest. Information of this type is rare (*4*). The results obtained help to answer the general question posed above. We report data on phosphorus as it is the nutrient most likely to cause lake eutrophication (*5*) and has been shown by Schindler's (*6*) full-lake experiments to be the most limiting nutrient for algal growth in nearby Canadian lakes of the same nature.

The Little Sioux wildfire burned 6000 ha of wilderness forest in the Superior National Forest of northeastern Minnesota during 14 to 17 May 1971, before it was extinguished by a 500-man task force and a rain and snow storm (*7*). It was the first major fire in this area for more than 60 years. After spreading from logging slash it burned lake watersheds covered with virgin, mixed stands of black spruce (*Picea mariana*); red, white, and jack pines (*Pinus resinosa, P. strobus,* and *P. banksiana*); balsam fir (*Abies balsamea*); and hardwoods, including red maple (*Acer rubrum*), aspen (*Populus grandidentata* and *P. tremuloides*), and birch (*Betula papyrifera*).

Because the Little Sioux wildfire was unplanned, prefire monitoring was impossible. We studied the effects of the fire by monitoring phosphorus concentrations in water moving in the burned watershed (133 ha) of Meander Lake and, simultaneously, in the unburned analog watershed (59 ha) of Dogfish Lake. The two lake watersheds, on the Vermillion Precambrian granite batholith (*8*), are similar in terms of vegetation, topography, and soil. Soils have developed in shallow depressions on the thin ground moraine of the Rainy Lobe of the Recent Wisconsin ice sheet (*9*). Granite outcrops and boulders are common, and the heat of the fire caused their exfoliation. These oligotrophic lakes are similar in area (Meander Lake, 36.0 ha; Dogfish Lake, 29.1 ha), average depth (5 m), and average water chemistry (Ca, 2.0; Mg, 0.7; K, 0.5; and Na, 0.6 mg/liter; electrical conductivity, 20 µmho/cm; *p*H 5.7 to 6.1). Mean annual precipitation in the area is 71 cm, about 64 percent falling as rain in the frost-free period of May to September. The mean temperature is 17°C in July and -15°C in January (*10*).

Natural precipitation and throughfall (water falling through tree crowns) were sampled with plastic funnels and bottles. Overland flow was sampled with small plastic troughs (2.5 cm wide and 30 cm long). Soil water was sampled with ceramic suction cups located at depths to 75 cm, depending on the depth of the soil profile. Water samples were collected during the snow-free season every 2 weeks at 20 points in each watershed in 1971 and 1972, and monthly at 10 points in 1973. Collection points were located at 150-m intervals along transects 30 to 50 m upslope and parallel to the lakeshores.

Total phosphorus in each sample was determined by the phosphomolybdate method with ascorbic acid reduction (*11*), after digestion of the sample with potassium persulfate for 45 minutes in a pressure cooker. Relative amounts of phosphorus (Table 1) were calculated by multiplying the phosphorus concentration by the volume of each sample, averaging for each water component and year, and then expressing the difference between the values for the burned (B) and unburned (U) watersheds as a percentage [that is, 100 × (B - U)/U]. The same formula was used to calculate relative volumes of water (Table 1).

The fire caused an increase in the volume of throughfall in the second and third years (Table 1) as the destruction of the tree crowns reduced rainfall interception, but concentrations and total amounts of phosphorus in throughfall in the burned watershed dropped over the 3-year period (Tables 1 and 2).

The volume of overland flow in the burned watershed increased and peaked in the second year (Table 1) because of the destruction of the transpiring trees and of much of the thick forest-floor layer. There was also a significant increase in phosphorus in overland flow in the first year (Table 1). However, the phosphorus concentration of overland flow at the burned site declined in the second and third years (Table 2), and 59 percent less phosphorus was released from the burned site compared to the unburned control site in the third year (Table 1). During the first 2 years after the fire, readily soluble phosphorus was leached from the ash and burned vegetation or absorbed by the regenerating understory.

The phosphorus concentration of soil water also increased after the fire (Table 2), but the increase relative to the control area peaked during the second year rather than the first (Table 1). Soil water volumes, initially much higher in the burned watershed, approached control values with time after the fire.

However, the increased phosphorus in the runoff water from the burned watershed had a negligible effect on the phosphorus concentrations of the adjoining lake and its input stream. Wright *et al.* (*12*) also found a negligible phosphorus input to Meander Lake after this fire. They calculated that the 1972 phosphorus loading of the lake was only 25 $\text{mg/m}^2$, and the estimated 40 percent increase due to the fire was within the expected yearly variation. They also found no differences between the algal flora of Dogfish and Meander lakes and concluded that the Little Sioux wildfire had little limnological effect.

Thus, as water moved from the terrestrial to the aquatic environment, the phosphorus concentration dropped markedly (Table 2). The explanation for this is fourfold.

Table 2. Phosphorus concentrations (parts per billion) of water, during the snow-free season, from the unburned watershed of Dogfish Lake (U) and the burned watershed of Meander Lake (B) after the Little Sioux wildfire in northeastern Minnesota, 14 to 17 May 1971.

| Year | Phosphorus (ppb) in | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Precipitation | Throughfall | | Overland flow | | Soil water | | Streams | | Lakes | |
| | U | U | B | U | B | U | B | U | B | U | B |
| 1971 | 40 | 200 | 183 | 654* | 1881* | 106* | 543* | 9 | 22 | 9 | 12 |
| 1972 | 36 | 240* | 127* | 1433 | 841 | 43* | 179* | 33 | 52 | 9 | 9 |
| 1973 | 37 | 142 | 93 | 1274 | 666 | 89 | 93 | 36 | 30 | 25 | 20 |

*Difference between U and B significant at $P = .05$.

1) Overland flow is a negligible fraction of total runoff and is transient and discontinuous (*13*). Subsurface flow is in intimate contact with the soil, and phosphorus is immobilized in the soil. This process has been confirmed for a number of chemical elements in laboratory column experiments with Minnesota forest soils (*14*).

2) Large portions of both watershed areas are lake surfaces (33 percent for Dogfish Lake and 21 percent for Meander Lake). Thus, inputs to the lakes from runoff are considerably diluted by precipitation falling directly on the lake surfaces.

3) Input stream waters are also diluted by the relatively large volume of lake water (for example, in the unburned area over the study period, the mean phosphorus concentrations of the input stream and lake were 26 and 14 parts per billion, respectively).

4) The fire occurred in early spring and vegetative regeneration was vigorous immediately after it [in one area just 5 months after the fire 190,270 new aspen suckers and 5,830 aspen seedlings per hectare were recorded (*15*)]. The prolific vegetative growth used some phosphorus released by burning and thus reduced losses to the aquatic environment.

Although our results are favorable for implementation of controlled burning in the study area, we stress that they should be used with caution. The Little Sioux wildfire occurred in early spring, just before the last snowfall, before new vegetative growth had begun, and when the forest floor was still cool and moist. The topography of the study area is not steep and practically no erosion occurred following the fire. The burned litter had no noticeable hydrophobic effects that might have inhibited water infiltration into the soil. A fire in summer or early fall might burn more intensely, exposing mineral soil to erosion and preventing recycling by vegetative uptake. The latter type of fire, or a fire in a large watershed with a small lake, might have detectable limnological effects. The effects of a forest fire on recycling processes differ with time of burning, topography, vegetative cover, soil type, relative size of the watershed and lake, and climate. Further studies are required to elucidate the relative importance of such factors, so that forest management policies involving fire can be wisely made and safely implemented.

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# Stratospheric Nitric Oxide: Measurements during Daytime and Sunset

Abstract. *Measurements of the temporal variation in the stratospheric nitric oxide concentration covering a time period from 11:00 to 20:30 local time show the effect of solar ultraviolet sunset. The experimental results strongly support the theorized role of nitric oxide as a catalyst in the destruction of ozone and its importance in the stratospheric ozone balance.*

The importance of NO as a catalyst in the stratospheric $O_3$ balance has been discussed by several authors (*1*). Measurements of stratospheric NO concentrations to validate the conclusions of these theoretical models are difficult because of its rather low concentration. In addition, to make a proper comparison between theory and the experimental measurements, it is important to have the NO measurements as a function of solar elevation. It is known that NO enters into the stratospheric $O_3$ balance through the interaction of atomic oxygen and of the solar ultraviolet (UV) radiation with $NO_2$ via the following processes:

$$NO_2 + O \rightarrow NO + O_2 \qquad (1)$$

$$NO_2 \xrightarrow{h\nu} NO + O \qquad (2)$$

and

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3)$$

where h$\nu$ is a photon. The reactions described in Eqs. 1 and 2 lead to the generation of NO when the solar UV radiation acts on the constituents of the stratosphere, whereas the reaction in Eq. 3 acts to remove the NO. Thus time-dependent measurements of NO (or $NO_2$) can provide a very important check of the models of the stratospheric $O_3$ balance in which the nitrogen oxides are considered to be effective catalysts for the destruction of $O_3$.

In our earlier report we described measurements of stratospheric NO, using the technique of opto-acoustic (OA) spectroscopy with a tunable spin-flip Raman (SFR) laser (*2*). Measurements were carried out during a balloon flight on 19 October 1973 from Palestine, Texas, and the measurements lasted from about 7:00 to 14:00 hours local time. This gave us the variation in the NO concentration from just before the sunrise till early afternoon. These experiments were terminated at 14:00 local time because of a battery failure. The measured noontime NO concentration of $2 \times 10^9$ molecule cm$^{-3}$ at an altitude of 28 km is in reasonable agreement with the recent spectroscopic measurements of NO in which the sun was used as the source of blackbody radiation (*3*). Reasonable agreement also exists between the maximum NO concentration measured by us and that obtained recently by chemiluminescence measurement techniques (*4*) at lower altitudes. Our in situ measurement technique, however, has the singular advantage of making possible NO measurements regardless of the solar elevation. Thus our measurement technique is particularly well suited for the exploration of the diurnal variation in the kinetics of the NO in the stratosphere. The measurements from our first balloon flight (which was carried out in close collaboration with Sandia Laboratories) gave us the predawn, sunrise, and midmorning data on the NO concentration at 28 km. These measurements confirmed the importance of the reactions described in Eqs. 1 and 2. How-