mented into several areas with the incursion of ocean water into Hudson Bay (*14*). Changes in the proportions of land, water, and ice, with related changes in albedo and energy balance, resulted in the development of the present circulation patterns and storm frequencies. The development of the prairie communities in the Great Plains by 9000 to 8000 years ago was apparently related to dry Pacific air reaching the Great Plains for the first time (*15*). The transition from woodland to desert or grassland throughout the southwestern deserts 8000 years ago was probably the result of the shift of the Aleutian low and the winter storm track into their present northerly position, resulting in less winter precipitation.

Late Pleistocene pluvial climates in the southwestern United States were generally contemporaneous with glacial climates in the northern part of the continent. The dry playa lakes in the Southwest contained water when the glaciers were well developed. The existence of continental glaciers modified general circulation patterns and caused pluvial southwestern climates. With a shift from glacial to nonglacial climates, continental glaciers took thousands of years to recede because of the large amounts of energy required to melt the ice. Changes in pluvial climates would lag behind changes in glacial climates as long as the glaciers existed. The relatively xeric woodland between 11,000 and 8000 years ago in the Southwest may have occurred in such a lag period. Postpluvial conditions finally dried the playa lakes and allowed the formation of desert and grassland communities after 8000 years ago, when heavy winter precipitation diminished in the Southwest.

An important inference from this interpretation is that winter precipitation was probably the most important climatic parameter affecting late Wisconsin and early Holocene plant distributions in the Southwest. This is not to say that temperature regimes, such as mild winters and cool summers, were not important. Another implication is that the effect of late Pleistocene winter pluvial climates had a southerly limit, and desert refugia should have been in Mexico. Fossil middens from the northern Mexican deserts could be used to test this inference. Related cultural inferences would be that the Paleo-Indians of the southwestern United States lived in mesic woodlands and grasslands and that cultural transitions from Clovis to Folsom to Desert Archaic cultures may have been related to transitions in climate and vegetation. Finally, since the last transition to desert climates and vegetation was about 3000 years later than the extinction of large mammals such as mastodon, mammoth, horse, and camel 11,000 years ago (*16*), changes in climate or vegetation are unlikely to have caused extinction.

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Conservation of Potassium in the *Pinus resinosa* Ecosystem

Abstract. *Rubidium-potassium ratios were determined on foliage, litter, and surface soils of plots in two plantations of* Pinus resinosa *41 to 46 years old previously fertilized once with potassium. Calculations based on indigenous soil rubidium as the "tagging" ion demonstrate that after 9 years some 60 percent of the foliage potassium is still derived from the fertilizer, and after 23 years about 40 percent of the foliage potassium is derived from the fertilizer. Additional fertilizer potassium is present in soil and litter, indicating the high retention of this mobile element in the pine ecosystem.*

The soil compartments and fluxes of forest nutrient cycles are poorly quantified but only in part because of the long times and large variabilities involved. Nutrient sources and sinks throughout the tree rooting volume are not readily measured, and thus attempted mass balances for the entire system do not reliably describe circulation within the soil. Few tracers are suitable for long-term studies. Use of radioactive Cs has illuminated several aspects of the short-term circulation of cations, but the minute quantities are tightly sorbed by clay minerals and cannot duplicate the behavior of its congener K (*1*).

We have used the "reverse tracer" technique of Hafez and Stout (*2*) to follow the fate of added K in simple ecosystems of *Pinus resinosa* Ait., red or Norway pine. Plantations of this species on formerly cultivated sandy outwash soils in northern New York State commonly display symptoms of acute K deficiency. Deficient stands respond to single applications of K fertilizers by marked increases in canopy density and by height and diameter growth (*3*). Surprisingly, growth responses to single applications of K (112 kg/ha) have continued for more than 25 years (*4*).

Such prolonged response can plausibly be attributed to efficient recycling of the added K. An alternative hypothesis is "pump-priming" by the initial fertilization; that is, recovery from acute deficiency might result in intensive exploitation of subsoil layers, which often contain "reserve" K (80 to 300 mg per kilogram of soil) extractable by treatment with boiling 0.5N or 1N HNO_3 (*5*, *6*). Roots of vigorous pines penetrate to depths of 2.5 m or more in many of these soils (*6*, *7*). Until now there has been little basis for choosing between these two hypotheses.

The reverse tracer technique is applicable because the Rb/K ratios of commercial K fertilizers, chlorides or sulfates, are generally one to three orders of magnitude lower than the corresponding ratios in unfertilized soils. Thus, additions of fertilizer lower the Rb/K ratio in the root environment. Since plant roots discriminate little in the uptake of the two elements (*8*), the proportion of total K derived from fertilizer in any specific tissue may be estimated from its Rb/K ratio provided (i) that the Rb/K ratio of an unfertilized control is also known and (ii) that the Rb content of the K fertilizer is either known or may be assumed negligible (*9*). The same constraints apply to estimates for litter or soil extracts.

We experimentally treated two well-stocked plantations displaying foliar evidences of K deficiency at ages of 23 (Russia, New York) or 34 (North Lawrence, New York) years (*10*). Commercial KCl at rates sufficient to supply 112 kg of K per hectare was broadcast on fully randomized plots in simple with-and-without trials. Twenty-three and 9 years later, respectively, we determined the Rb and K concentrations in foliage of three ages, and of litter and surface soil (15-cm depth) samples (*11*) (Table 1). Calculation from Rb/K ratios (*8*) reveals that some 40 or 60 percent of the foliar K in treated trees at the two locations, respectively, is still attributable to the original fertilizer application. Data from other locations indicate additional storage in wood and bark.

Plants already well supplied with K may take up some amount of added K without necessarily increasing the total foliar concentration of the element (*2*). At Russia, foliar K concentrations of fertilized and control trees did not differ significantly at either 5 or 23 years after treatment; both were above the concentration at which growth response would be expected (*3*), despite initial indications of slight deficiency. In contrast, at North Lawrence foliar K concentrations show that the controls are clearly deficient (*3*) whereas the treated trees are still adequately supplied after 9 years.

The Rb/K ratios are known to differ with tissue and tissue age within the same plant (*12*). Such differences between the first season and older foliage in our material (Table 1) are at present unexplainable, but they do not materially alter the estimated proportion of leaf K derived from fertilizer. The Rb/K ratios in plants are not closely related to the ratios of either the exchangeable or the extractable elements in soil, even in pot cultures with homogeneous soil and confined root systems (*2*). It is likely that some fertilizer K penetrated below the surface layer at North Lawrence because of the low exchange capacity, 4.2 to 5.0 meq per 100 g (in unbuffered $CaCl_2$) as contrasted with 11 to 17 meq at Russia. Nevertheless, the resulting differences in soil K retention and supply at the two locations have not greatly influenced the persistence of added K in the foliage.

Table 1. Mean K concentrations and Rb/K ratios (in millimoles of Rb per mole of K) of foliage, litter, and surface soil, with the calculated percentage of K (in italics) derived from a single application of fertilizer 9 or 23 years before. Litter values are corrected for included soil.

Sample	Foliage						Litter		Soil, 0 to 15 cm (extractable with 1N HNO_3)	
	1st year		2nd year		3rd year					
	K (%)	Rb/K	K (%)	Rb/K	K (%)	Rb/K	K (%)	Rb/K	K (mg/kg)	Rb/K
Russia; treated age, 23 years; sampled age, 46 years (n = 3)										
Control	0.47	5.79	0.39	2.62	0.41	2.16	0.085	4.25	61	4.82
K, 112 kg/ha	0.49	3.36*	0.41	1.67*	0.37	1.60*	0.092	2.54*	60	2.22*
% K from fertilizer		*42*		*37*		*26‡*		*41*		*54*
North Lawrence; treated age, 34 years; sampled age, 43 years (n = 2)										
Control	0.61§	9.20	0.29	3.66	0.27	2.49	0.052	4.23	14	5.18
K, 112 kg/ha	0.76†§	3.54*	0.38	1.33*	0.34†	0.95*	0.055	3.35*	16	4.66*
% K from fertilizer		*62*		*64*		*62*		*21*		*10*

*Significantly different from the control at 1 percent, according to the t-test. †Significantly different from the control at 5 percent, according to the t-test. ‡Value for 4th-year foliage, based on only two replications, is 40 percent. §Values are high because the foliage is immature.

Although some K is withdrawn from senescent foliage before abscission, external cycling by leaf fall and canopy leaching approximates 10 to 15 kg ha^{-1} $year^{-1}$ in this species (*13*). The total K content of the entire litter layer is also about 10 to 15 kg/ha (*14*), or a single year's return. It is likely that reabsorption by the intense fine root net (*15*) overrides differences in retention by litter or surface mineral soil.

Of the fertilizer K applied (112 kg/ha) at Russia, some 45 to 50 kg is still present in the surface soil. A conservative estimate of the K in foliage and litter is 25 kg, leaving only 35 to 40 kg to be accounted for in wood, bark, and branches, plus whatever leaching may have occurred during the 23-year period. Thus it appears that the added K has been conserved with extraordinary efficiency, even on this freely drained, strongly acid fine sand.

Preliminary data from forest-grown *Picea glauca* (Moench) Voss and *Picea rubens* Sarg., white and red spruce, fertilized with K 5 years before, indicate foliar retentions comparable to that for *Pinus resinosa*. Although numerous questions about soil pools and distributions of Rb and K within the tree are yet to be examined, the relative simplicity, economy, and safety of the Rb reverse tagging technique suggest a wider applicability of this technique in long-term studies of terrestrial nutrient cycles.

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$$100 \cdot \frac{\left(\frac{Rb}{K}\right)_c - \left(\frac{Rb}{K}\right)_f}{\left(\frac{Rb}{K}\right)_c}$$

where the subscripts c and f represent control and fertilizer, respectively; Rb is in millimoles, and K is in moles (*2*). The estimation assumes essentially no Rb in the fertilizer; the presence of the maximum amount of Rb observed by Hafez and Stout (*2*) would increase the calculated value by only 1 percentage point.

10. The experimental plots were established on New York State forests near the locations named. The Russia stand was on Hartland loamy, very fine sand; at treatment it was 23 years old and averaged 9.4 m high with 1280 stems per hectare immediately after a thinning of about 10 percent. Plot size was 0.08 ha, with three replications. Foliar symptoms of K deficiency were slight. The North Lawrence stand was on Croghan loamy sand; it was 34 years old when treated and had an average basal area of 18.8 m²/ha with 1430 stems per hectare 2 years after light thinning. Plot size was 0.12 ha with two replications.
11. North Lawrence samples were collected on 23 June 1976; Russia samples, on 25 September. The Rb and K in oven-dried foliage and litter samples were determined according to the method of A. A. R. Hafez, J. R. Brownell, and P. R. Stout [*Commun. Soil Sci. Plant Anal.* **4**, 333 (1973)], except that K rather than Cs was used to suppress interference in the Rb determintion by atomic absorption, and K was determined by flame spectrophotometry.
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Clustering Hypothesis of Some High-Temperature Superconductors

Abstract. *Cluster formation in metallic crystal lattices is important for most high-temperature superconductors.*

The concept of intermetallic bonding in inorganic compounds has been a favorite subject in materials science for many years. The existence of intermetallic bonding or metal-to-metal bonding leads to entirely new structures, particularly among the transition metal compounds. In these structures the metal-to-metal bonding manifests itself by the formation of clusters within the metallic lattice such as triangles, tetrahedra, octahedra, chains, and pairs (*1*). One of the first inorganic transition metal cluster compounds discovered was hydrated $MoCl_2$, whose structure contains octahedra of molybdenum atoms (*2*). Van Arkel (*3*) was one of the first to point out the importance of metal-to-metal bonding as a general phenomenon in the field of inorganic chemistry and used this concept as a perturbation to understand the stability of inorganic compounds. Metal-to-metal bonding was then discovered among numerous transition metal halides (*4, 5*) and resulted in a field of intensive study in organometallic chemistry (*6*).

In all these metal cluster compounds, whether they are typically ionic or organometallic, the metal-metal distance in the cluster—the intracluster distance—is about the same as that in the element. The distance between the clusters—the intercluster distance—varies greatly, depending on the type of compound involved, but is much larger than the metal-metal distance in the element. These intercluster distances have a strong impact on the physical properties of the compound. In the organometallic cluster compounds the distances between the clusters, which are pushed apart by the organic groups, are so large that the metal clusters show localized behavior. However, in numerous inorganic compounds such as the chalcogenides and phosphides, the intercluster distances, although larger than the distances in the metal, can still be metallic distances, resulting in metallic conductivity.

This cluster hypothesis of short and also long (but still metallic) distances now appears to be an important feature for a number of superconducting structures with high transition temperatures (T_c's). It is not altogether a new idea and had been pointed out previously for one structure or another (*7*). The systematic occurrence of metal clustering in high-T_c superconducting compounds, however, was first observed in the ternary sulfides $MeMo_6S_8$ (where Me stands for tin, lead, and so on) (*8*); molybdenum clusters into octahedra with short distances of ~ 2.70 Å and intercluster but still metallic distances of 3.26 Å, about 16 percent larger than that in the element. We then observed that similar clustering of the metal lattice occurs in other high-T_c superconductors such as hexagonal MoN (*7*) and the cubic β-tungsten or A-15–type compounds. In MoN three of every four molybdenum atoms cluster into triangles (Fig. 1), and in the A-15 phases the metal atoms, such as niobium, cluster into chains with long but still metallic distances between the clusters (Table 1). The recently discovered new series of high-T_c superconducting compounds $MeRh_4B_4$ (where Me is a transition or rare earth element) is another example of their clustering behavior (*9, 10*). In this structure the rhodium atoms cluster into sheets of tetrahedra with a distance of ~ 2.70 Å; the sheets are interconnected through a long but still metallic distance of 3.14 Å (Fig. 2). The high-T_c superconducting materials $(Th, RE)_2C_3$ (where RE is a rare earth element) crystallize in the body-centered Pu_2C_3-type structure (*11*). No clearly separated clusters occur in this structure, but the metal lattice does distort into a lattice of shorter (3.35 Å) and longer (3.70 Å) metallic distances. It is difficult to state whether there is direct metal-metal bonding between plutonium atoms.

In all these superconducting structures with high transition temperatures an essentially three-dimensional metal lattice is maintained, the metal-metal distances

Table 1. Intra- and intercluster distances ($Me\text{-}Me_{IA}$ and $Me\text{-}Me_{IR}$, respectively) in some high-T_c superconducting (SC) and nonsuperconducting (NSC) cluster compounds.

Compound	$Me\text{-}Me_{IA}$ (Å)	Metallic $Me\text{-}Me_{IR}$ (Å)	Type and dimensionality of metallic cluster lattice	Nonmetallic $Me\text{-}Me_{IR}$ (Å)	Element Me-Me (Å)	Electrical properties
MoN	2.67	3.00	Triangles, three-dimensional		2.73	Metallic, SC
Nb_3Sn	2.64	3.24	Chains, three-dimensional		2.86	Metallic, SC
$PbMo_6S_8$	2.57–2.74	3.26	Octahedra, three-dimensional		2.73	Metallic, SC
YRh_4B_4	2.63–2.75	3.14	Sheets of tetrahedra, three-dimensional		2.69	Metallic, SC
Mo_2S_3	2.85–2.87	3.22	Zigzag chains, two-dimensional	4.10	2.73	Metallic, NSC
VMo_2S_4	~2.85	~3.28	Zigzag chains, two-dimensional	~4.00	2.73	Metallic, NSC
$Ga_xMo_2S_4$	2.84		Tetrahedra, isolated	4.05	2.73	Semiconducting, ferromagnetic
$ReSe_2$	2.65–2.93	3.08	Planar Re_4 groups, one-dimensional	3.92–4.12	2.76	Semiconducting, diamagnetic