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BARIUM AND MANGANESE TRENDS IN TREE-RINGS AS MONITORS OF SULFUR DEPOSITION¹

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Abstract. Barium and manganese concentrations in radial growth increments of heartwood from *Juniperus virginiana* L. are used to examine changes in soil reaction and sulfur deposition. Barium and Mn trends from trees growing on 2 sites with acid, low-Ca soils, signaled sulfur-induced changes in soil acidity after 1870, while Ba and Mn trends before 1870 did not. Factors controlling Ba availability are hypothesized to have changed from soil acidity before 1870 to precipitation of BaSO₄ by increased soil sulfate after 1870.

1. Introduction

Change in soil acidity can be brought about by both natural (Blanchar and Marshall, 1981; Spurr, 1940) and anthropogenic (Reuss and Johnson, 1986) factors. Differentiating the natural factors that change soil acidity such as nutrient sequestering, climate, and vegetation type, from anthropogenic factors such as increased acid deposition presents a significant problem. Soil acidification by sulfate acids, although not uniquely anthropogenic, is a regional process resulting from industrial sulfur emissions. An earlier paper linked increased sulfur levels in wood with industrial activity (Guyette *et al.*, 1989). In this paper, we present evidence to support the hypothesis that soil acidification caused by the deposition of sulfur compounds can be separated from acidification due to other causes by comparing concentrations of manganese and barium in tree-rings.

Central to this paper are soil reactions controlling Mn and Ba concentrations in the soil solution. The solubility of most Mn minerals in soil increases rapidly with decreasing soil pH (Lindsay, 1979). This increase in solubility can result in elevated Mn concentrations in the soil solution if a sufficient quantity of Mn mineral is available to support a higher equilibrium. A reaction relating Mn⁺² activity in the soil solution to pH for a common soil Mn mineral such as manganite is (Lindsay, 1979; Barber, 1984):

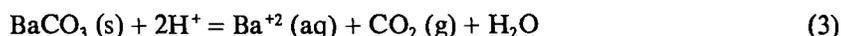
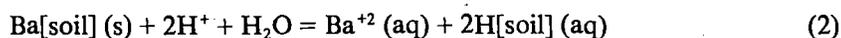
$$\log_{10} \text{Mn}^{+2} (\text{aq}) = 8.65 - 2\text{pH} . \tag{1}$$

Note that the potential Mn⁺² concentration goes up 100 times (two log₁₀ units) for each unit change in soil pH. Thus, pH has a great potential influence on solution

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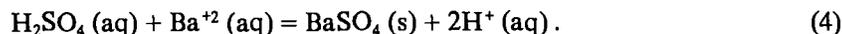
Mn concentrations. As predicted from the solubility of Mn minerals, soil pH is inversely correlated with increases in the Mn uptake and concentration of plants (Barber, 1984; Marschner, 1986; Sillanpaa, 1982) and trees (Gerloff *et al.*, 1966; McClenahan *et al.*, 1989). In eastern redcedar Mn concentrations in sapwood and heartwood are inversely correlated with soil pH (Guyette *et al.*, 1992b). These studies provide a strong case for the use of Mn concentrations in tree rings as a monitor of change in soil pH.

The soil chemistry of Ba is also central to the ideas presented here because its solution concentration and therefore potential uptake is controlled not only by H⁺ but by solution sulfate concentration. Like Mn, Ba concentrations in plants are also inversely correlated with soil pH (Menzel, 1954; Connor and Shacklette, 1975). Examples of soil reactions governing soil solution Ba⁺² concentrations are:



where [soil] = exchange site on clay particle.

The precipitation of Ba from the soil solution, on the other hand, is highly dependent on the activity of sulfate. The solubility product of BaSO₄ is 1.1×10^{-10} M², making BaSO₄ very insoluble. Because of this small solubility product, even minor increases in the SO₄⁻² activity of the soil solution will precipitate BA⁺² as BaSO₄. Indeed, Ba is used to test for the presence of sulfate (Wall *et al.*, 1980). The reaction precipitating BaSO₄ from the soil solution is hypothesized to be:



Reactions 1, 2, 3, and 4 can be used to link chronologies of Mn and Ba in tree rings with historical data on atmospheric emissions. The objectives of this research are to examine Ba and Mn levels in tree-rings of old eastern redcedar (*Juniperus virginiana* L.) as indicators of changes in soil chemistry caused by sulfuric acid. This research is part of a larger study on using tree-rings to monitor changes in environmental chemistry in the Ozark Region.

2. Materials and Methods

All trees used in this study grew on sites that had shallow, residual unclassified soils with exposed rhyolite or dolomite bedrock. Sites were xeric and generally steep with very well drained soils. Mean annual precipitation ranges from 92 to 112 cm. Spring is the wettest season and the season of cambial growth. In general, because of their low productivity, the sites have had little disturbance from logging. Because of the high surface to volume ratio, these soils are particularly sensitive to atmospheric input.

Trees were sampled on two substrates in each of two areas subject to high and low atmospheric sulfur emissions in Southeast Missouri. In both areas, trees were

TABLE I
Site, soil, and chronology data for redcedar sites

SO ₂ exposure ^a	High	Low	High	Low
Substrate	Rhyolite	Rhyolite	Dolomite + chert	Dolomite
Maximum soil depth (cm)	49	75	73	33
Average slope (degrees)	32°	25°	26°	32°
Soil pH				
A horizon	4.60	4.52	5.79	6.49
E horizon	4.18	4.05	5.34	6.44
B horizon	3.70	3.91	6.02	6.60
Range (all horizons)	3.4–5.8	3.2–6.0	3.7–7.2	4.5–7.9
Mean elevation (m)	320	289	259	243
# Trees in chronology				
(maximum)	14	10	15	15
(minimum) ^b	3	3	6	3
Total number 20 yr sections analyzed	114	88	110	132
Mean sapwood-heartwood boundary year	1959	1962	1959	1958
Mean heartwood Mn ($\mu\text{g g}^{-1}$)	16.7	13.9	3.69	2.86
Mean heartwood Ba ($\mu\text{g g}^{-1}$)	14.04	17.78	3.14	1.16
1st Order autocorrelations ^c				
Mn chronologies	0.50	0.12	0.66*	0.82*
Ba chronologies	0.70*	0.38	0.58	-0.44

^a Based on duration and distance from smelters (Winslow, 1894; Wharton *et al.* 1969), population centers and present-day SO₂ emissions (McLaughlin and Taylor, 1985).

^b Sample density varies decreases due to tree age, with minimums occurring before 1800.

^c * denotes significant ($P \geq 0.05$) 1st order autocorrelation.

sampled that grew on two soil types; acidic soils over rhyolite, and more neutral soils over dolomite. Data on these sites and trees is presented in Table I.

Live trees were sampled for chemical analyses by extracting a 17 mm diameter core from the tree bole. Cross sections were taken from dead trees. Reference cores were taken first with a 4 mm increment borer to determine the place of extraction for the large core and for later use in growth analysis and dating. Annual growth increments were crossdated (Stokes and Smiley, 1968) to insure the correct dating of the annual increments and assign dates to remnant (dead) wood. Cross-dating yields accuracy to the year and allows for the detection of false and missing rings. Dated 20 yr increments of wood were prepared from cores and single radii of cross-sections. The sapwood of each radius was sampled as a unit. The 20 ring (yr) sections from the heartwood were centered on odd decades.

The soil under each tree was sampled to estimate the bulk soil pH of the rooting environment. A soil auger was used to collect 50 g samples of soil. Composite samples were collected from each horizon and stored in labeled plastic bags in a freezer. After removing the litter layer, each of three soil horizons was sampled: an upper horizon with significant organic matter accumulation, typically an A hori-

zon (0–13 cm deep); an eluvial horizon, typically an E horizon (13–24 cm deep); and an illuvial horizon, typically an argillic B horizon (24–45+ cm deep). Horizons were distinguished by color, texture, and structure. The upper horizon was distinguished by a friable texture and organic matter darkening. The eluvial horizon was identified by its lighter hue and lack of organic matter. The lower illuvial horizon was identified by its darker hue (usually a dark red or brown) and high clay content. When distinct horizons were not visually identifiable, composite samples were taken at the surface (0–10 cm), midway to bedrock, and at bedrock. An effort was made to include soil from all rooting zones. Soil was thawed and was sifted through a #10 mesh screen before pH and Mn determinations were made.

Soil acidity was measured as pH with a glass Ag/AgCl combination electrode with a KCl reference electrode. Ten gram samples of soil were mixed with 10 ml of 0.01 M CaCl₂. The solution was then stirred at 10 minute intervals, and the pH was measured after 30 min. Individual horizon pH values were averaged together for each site to establish a mean pH. Simple arithmetic averaging of pH values was used to better reflect the soil profile acidity. Since the volume of the soil solution was not known and is highly variable by season, horizon, and site, estimating hydrogen ion concentrations (ions per unit volume) by logarithmic conversion was judged to be inappropriate. However, these arithmetic averages could be misleading if used for calculations of hydrogen ion flux.

Data on the soil chemistry and sites of sample trees is given in Table I. Additional data are available in earlier papers (Guyette *et al.*, 1992a, b).

Wood samples (0.5 to 1.0 g) were analyzed by inductively coupled plasma optical emission spectroscopy (ICP Scan). Samples were prepared for analysing using a nitric acid – perchloric acid digestion procedure. The ICP Scan was conducted with a Jarrell-Ash Model 1100 Mark III with 40 analytical channels, controlled by a Digital Equipment Company 11/23+ computer. The instrument was standardized with a series of seven standards containing 36 elements. The detection limit was obtained by taking ten integrations of zero standard; three times the standard deviation of the mean was used as the detection limit which was 0.03 $\mu\text{g g}^{-1}$ for Ba and 0.2 $\mu\text{g g}^{-1}$ for Mn (Guyette *et al.*, 1992a).

Eight element chronologies (4 each for Ba and Mn) were used for this study. They were constructed from dated, 20 year radial sections of eastern redcedar heartwood. Each consisted of 10 or more trees. One radius per tree was analyzed. Element series from each tree were standardized and combined into chronologies (Guyette *et al.*, 1989). Trees from 41 or more sites were used to establish the relationship between soil pH and concentrations of Ba and Mn in xylem.

Correlation analysis was used to associate soil pH with element concentrations and to relate Ba and Mn trends. Time series data, such as Ba and Mn trends in tree rings, are often autocorrelated. Valid statistical significance levels for correlation coefficients require that observations be independent. The sample size used in calculating significance levels of all correlation coefficients among Ba and Mn time series has been adjusted where significant first order autocorrelation

TABLE II
Correlation coefficients among element concentrations and soil pH for all sites

	ln [Ba]	ln[Mn]
Sapwood	-0.82 ^a (62)	-0.79 ^a (67)
Heartwood	-0.76 ^a (41)	-0.75 ^a (41)

^a All correlations significant at the $P \geq 0.01$ level. The number of samples is given in parentheses after the correlation coefficient.

diminished the effective number of observations (Fritts, 1976). Table I gives the first order autocorrelation for the base chronologies.

3. Results and Discussion

Ba and Mn concentrations in both sapwood and heartwood were found to be negatively correlated with soil pH (Table II). This is consistent with their availability as predicted by Reactions 1, 2, and 3. Therefore, positive correlations among Ba and Mn concentrations between temporal series of tree-rings were expected because of the negative correlation of both Ba and Mn in xylem with soil acidity (Table II). As expected, Ba and Mn chronologies are positively correlated, although not significantly, for trees growing on rhyolite substrate during the pre-industrial era (i.e. before 1870; Figure 1, Table III). It is important to remember that the use of dates in this paper refers to the 20 yr period centered on odd decades. Therefore, the 1870 date of the pre-industrial era actually is the period from 1860 to 1879.

Recent divergence of Mn and Ba trends in Figure 1, beginning circa 1870, supports the proposed hypothesis that sulfate begins controlling Ba concentrations in the soil solution. Evidence for increasing sulfur deposition is present in tree rings (Guyette *et al.*, 1989, 1991) and in the production levels of minerals containing S produced in Missouri (Wharton *et al.*, 1969). For example, the production of high S coal in Missouri increased by a factor of 10 from 280 000 tons in 1860 to 3,017,285 tons in 1892. Emissions from the production of lead from galena (13.4% S content) increased from 3 159 tons per year in the 1860's to 44 546 tons yr⁻¹ in the 1890's. In addition, the increased production of iron, copper, and barite added to emissions of S. Figure 2 illustrates the similarity between S levels in radial growth increments found in an earlier study and the ratio of Mn and Ba chronologies from both rhyolite sites. Table III gives correlation coefficients by chronology and time period for trees growing on rhyolite bedrock. We propose that this divergence signals a change from H⁺ control of Ba in the soil solution to precipitation by an increased sulfate equilibrium in the soil solution. In other words, the reactions controlling Ba concentration in the soil solution changed from Reactions 2 and

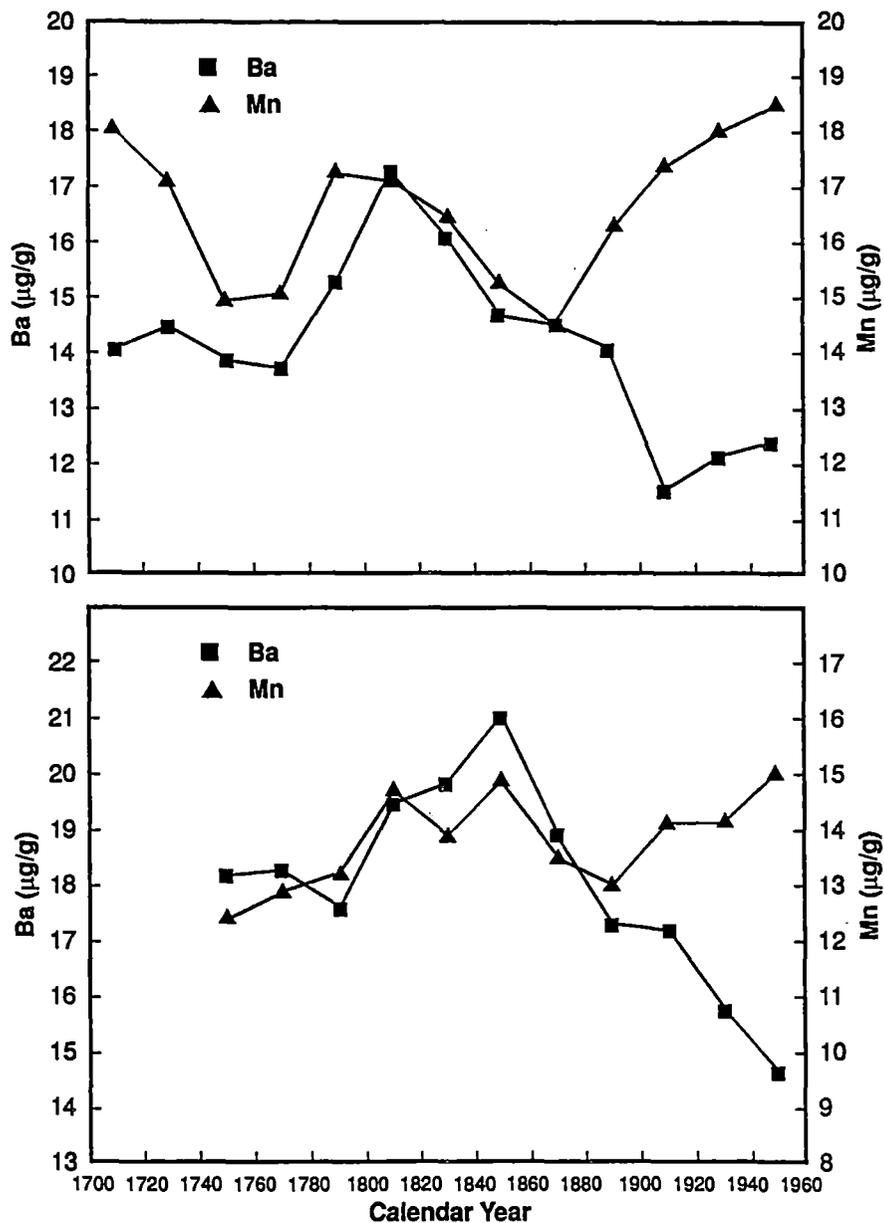


Fig. 1. Manganese and Ba chronologies for trees growing over rhyolite-derived acid soils. The top set of chronologies is for sites with high sulfur exposure, the lower is for sites with low sulfur exposure.

3 to Reaction 4. To simulate the change in mechanisms controlling Ba availability through time from Reactions 2 and 3 to Reaction 4, the Ba normalized chronologies were multiplied by an indicator variable (+1, from 1700 to 1859; -1, from 1860 to 1960) to reflect increases in the soil sulfate equilibrium. This resulted in the significant and positive correlations shown in Table III among Mn

TABLE III

Correlation coefficients between Ba and Mn chronologies from rhyolite sites with differing exposure to sulfur emissions. The number of 20 yr pairs is given in parentheses after each correlation coefficient^b

Chronology pair	Pre-industrial	Post-industrial
	1700-1879	1880-1960
Ba1 × Mn1	+0.39 (9)	-0.83 (4)
Ba2 × Mn2	+0.84 ^a (7)	-0.82 (4)
	1700-1960 ^c	
Ba1 × Mn1	+0.56 ^a (13)	
Ba2 × Mn2	+0.85 ^a (11)	

^a Indicates significance at the $P \geq 0.05$ after adjustment for 1st order autocorrelation.

^b Ba1 = Ba chronology, high sulfate exposure.
Mn1 = Mn chronology, high sulfate exposure.
Ba2 = Ba chronology, low sulfate exposure.
Mn2 = Mn chronology, low sulfate exposure.

^c These correlation coefficients are for normalized Ba chronologies which have been multiplied by an indicator variable (+1, from 1700 to 1859; -1, from 1860 to 1960) to reflect the hypothesized change from reactions 2 and 3 to 4 in controlling Ba⁺² in the soil solution.

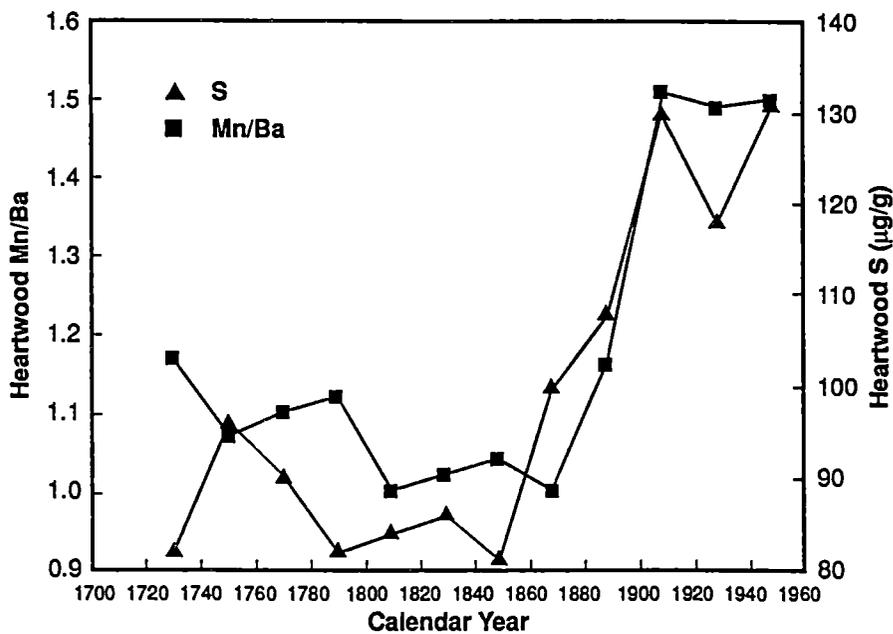


Fig. 2. The ratio of Mn and Ba chronologies from 24 trees growing in acid soils over rhyolite bed-rock compared to S concentrations in an independent set of trees from the Ozark area (Guyette *et al.*, 1989).

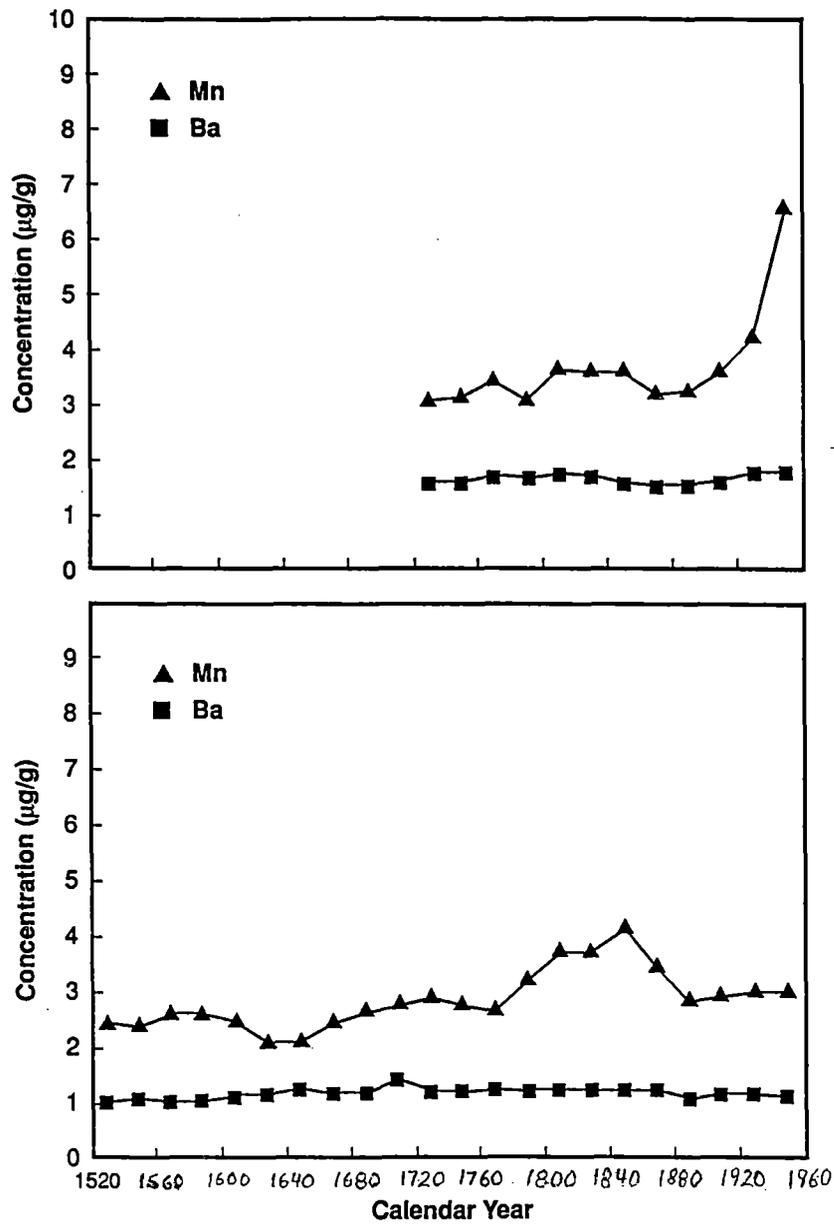


Fig. 3. Manganese and Ba chronologies derived from trees on high Ca, near-neutral soils over dolomite. The top set of chronologies is for sites with high sulfur exposure, the lower is for sites with low sulfur exposure.

and Ba chronologies from both sites for the whole time period.

No significant correlations were found between Ba and Mn chronologies from trees growing on dolomite sites. Although recent increases in Mn are apparent for one of these sites, it is not accompanied by a coincident reduction in the Ba

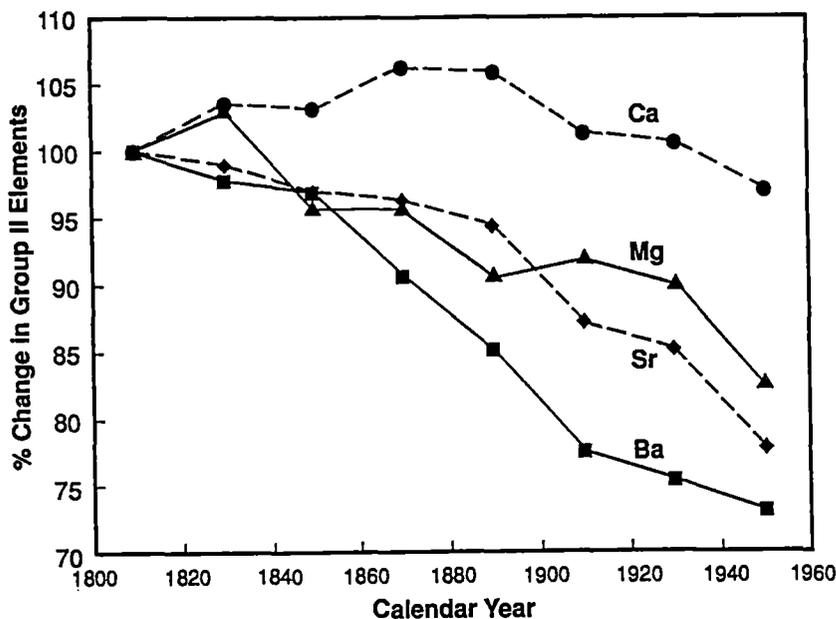


Fig. 4. Percentage change in concentrations of Group II cations in growth increments of 24 eastern redcedar from rhyolite sites. Percent values are based on 1800-1819 concentration of each element.

concentrations. These trends are illustrated in Figure 3. The lack of a clear and recent reduction in xylem Ba among the element chronologies from dolomite sites is not consistent with our hypotheses and clearly limits the use of Mn-Ba trends to acid, low-Ca soils. What is consistent, however, is the similarity between the 2 chronologies from trees on dolomite soils versus the similarities between the 2 chronologies from trees on rhyolite soils. This adds weight to the argument that soils are controlling Ba and Mn trends in tree-rings.

Differences between dolomite and rhyolite derived soils relative to sulfur deposition are to be expected, however, and may be due to several different factors. The differential weathering rates of dolomite and rhyolite may greatly alter Ba input to the soil. The chemistry of the high Ca-lower acidity soils may influence Ba soil reactions. For instance, BaOH_2 is soluble and likely to exist in 'high' pH soils where it will not react with sulfate because of the strong hydration by OH^- groups. High Ca concentrations may precipitate sulfate as gypsum and buffer increases in soil sulfate equilibrium. Also, Ba in xylem produced on these high pH soils is very low in concentration to begin with. This may reflect a low concentration of Ba in the soil solution. Plant uptake of Ba may be limited to the interception of Ba on exchange sites by root growth.

Soil leaching of Ba from increasingly acid precipitation is an alternative hypothesis which might explain the recent reduction in Ba concentrations in redcedar growth increments from rhyolite sites. Loss of Group II cations such as Ba, due to leaching might be expected on these steep rhyolite sites with shallow soils. Figure 4 illustrates

the decline of Ba in radial growth increments of 24 redcedar trees from rhyolite sites relative to the other Group II elements, Ca, Mg, and Sr. This figure illustrates two important points. First, there is a decline in Mg, Sr, and Ba that is consistent with the alternative hypothesis. Second, Ba concentrations have declined the most. The order of soil retention of divalent cations is $Mg < Ca < Sr < Ba$ (Bohn *et al.*, 1985). The availability of Ba and Sr should be affected the least by soil leaching. Thus, although the availability of Group II elements may be affected by leaching, the pattern of their decline in growth increments does not support the alternative hypothesis that leaching is the primary factor in reducing Ba availability in soils.

4. Conclusions

(1) Ba and Mn trends in tree-rings can be used as a signal for increases in soil sulfate activity on soils derived from rhyolite.

(2) The use of Ba and Mn trends as a sulfate signal does not work on high Ca circa neutral pH soils.

(3) Both Ba and Mn in redcedar xylem were inversely correlated with soil pH by site. Trends in Ba and Mn chronologies from rhyolite were similar before 1870 indicating non-sulfate related variability in soil reaction, whereas trends after 1870 diverge, coincident with increasing sulfur emissions from coal burning.

Trends in Ba and Mn in tree-rings may be useful in differentiating changes in soil acidity due to anthropogenic sulfur emissions from those changes in soil acidity due to natural, non-sulfate, acidification processes such as climate, base cation sequestering in woody vegetation, fire suppression, and species change.

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