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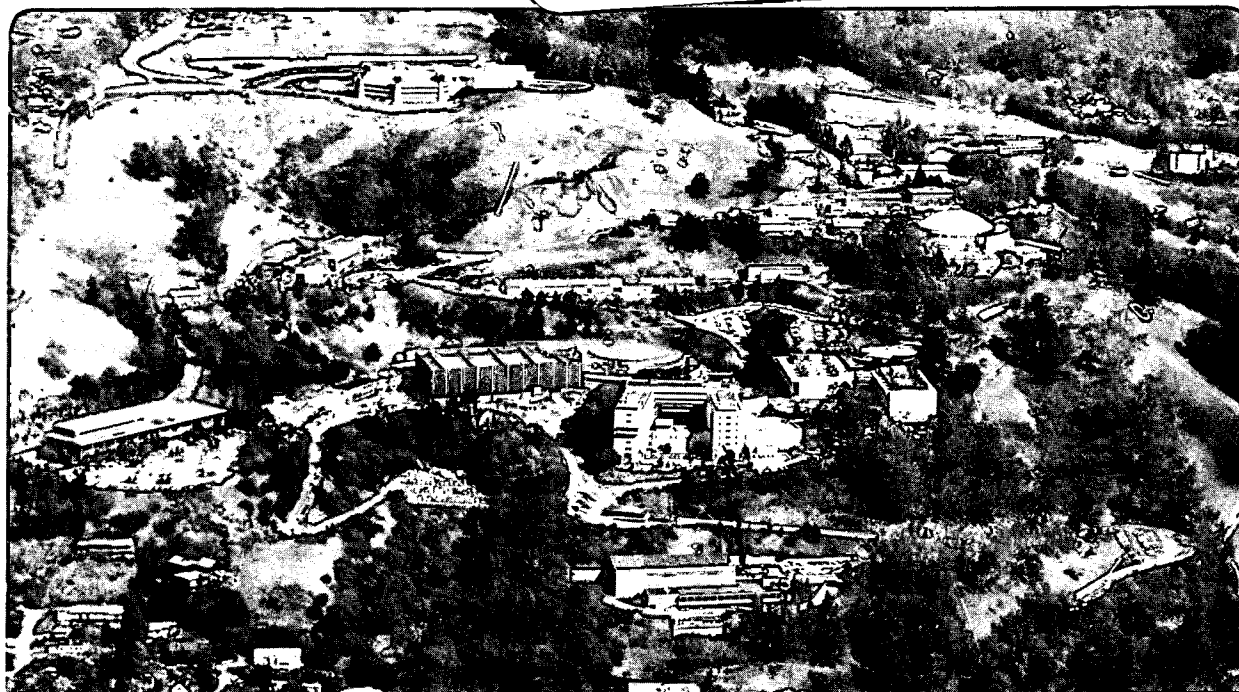
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Using Changes in Elemental Composition of Selected Plants as Earthquake Predictors

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Abstract

Based on reported changes in groundwater prior to earthquakes, an argument can be put forth predicting compositional changes in those plants dependent on groundwater, prior to earthquakes. Furthermore, concentrating activities of active ion transport mechanisms in the plant-water interface can 'amplify' changes occurring in the ground water ion mix, making measurements easier. Automated x-ray fluorescence analysis equipment currently available makes it practical to test these hypotheses on broad-leaf plants in selected areas.

Introduction

The search for ways to detect precursory earthquake phenomena has not excluded empirical observations, such as behavioral changes in animals. Empirically, other ecological phenomena may be as likely to produce positive correlations - specifically changes in plant material in the vicinity of imminent earthquakes. Such changes are not as easily observable as is animal behavior. However, as part of our development of a series of x-ray fluorescence analyzers for automatically monitoring particulate air pollutants, we have gained the ability to routinely and inexpensively monitor nutrient element levels in plant leaf material. Specifically, we can automatically unravel the concentrations of about 30 elements in thin samples, such as are naturally produced

as leaves in broad-leaf trees. Given this capability, we have attempted to develop a tentative rationale and procedure for testing the sensitivity of plant materials to earthquake precursory phenomena.

A cursory review of recently published efforts to accurately predict the time of occurrence and magnitude of earthquakes (Brace (1977), Mogi (1977), Press (1975), Wakita (1977)) reveals the active investigation of precursory phenomena which may be either primary results of pre-slip stress buildup or secondary results, transported via an intermediary such as groundwater. Primary phenomena include measurable changes in rocks being stressed to fracture - electrical resistivity changes, changes in wave velocities, changes in residual magnetism, etc. - and measurable changes around gouge and rock fracture surfaces prior to stick-slip phenomena - mainly preseismic creep. Groundwater level, turbidity and temperature changes as well as increases in radon in groundwater, depend on groundwater to transport effects of the primary phenomena. Precursory behavioral patterns in animals may be classified as secondary phenomena if animals are assumed to be responding, for example, either to preseismic creep or to the sounds of rock fracturing.

A potentially useful group of precursory phenomena, one not yet being investigated, is the measurement of ecological disruptions related to secondary phenomena. Changes in groundwater will normally have measurable effects on plant life dependent on groundwater supplies. Specifically, physical disruption of surfaces in contact with groundwater supplies can change the ratios of micronutrient ions in the water supply. Such changes may be 'amplified' and accumulate in plant cellular material. Amplification, a result of active ion transport mechanisms in the plant, and accumulation enhance our ability to detect minuscule changes in the water supply.

Trigger phenomena, such as lunar attraction or water injection into a faulting area, add still another dimension to the possibilities of successful

earthquake prediction, as do local faulting peculiarities of each susceptible region. It seems likely that the best probability of successful prediction will be had by the development of parameter values for use in key predictors; each predictor being unique for a particular region. We propose putting one more parameter into the equation; that of the elemental profile of plants dependent on groundwater emanating from active regions surrounding faults.

Expected Groundwater Changes

Evaporation and wind pickup from the oceans eventually falls back to the earth, where some percentage percolates into underground reservoirs, later emerging as spring or groundwater. (Duvigneaud (1975), Epstein (1972), Ovington (1965)) Wind pickup from ocean surfaces results in some redistribution of minerals from the ocean onto land masses. Water pickup of minerals from the air, from surface layers of the earth and from deeper earth structures eventually redeposits minerals into the ocean. Mineral cycling by these means is not uniform, depending on the chemical properties of the mineral and the long-term weather and vegetative ecology of the region into which it is deposited. Phosphorous, for example, tends to be lost to deep ocean sediments. In arid and semiarid regions, sodium chloride, sodium carbonate and sodium sulfate may accumulate because of inadequate leaching by rain. Recycling in such cases may await volcanic and/or seismic upheavals. Seismic disruption of crustal layers of the earth may disrupt existing water percolation channels or may create new ones resulting in short-term changes in mineral pickup by water on its way from rain to reservoir. Such concentration changes and the appearance of isotopic anomalies in groundwater have already been reported as possible precursory earthquake phenomena, as was observed by Wakita (1977).

Table 1 illustrates the approximate crustal concentration of elements. Concentrations in crustal material is orders of magnitude greater than the

average ionic concentration in North American lake and stream water. Under physically stable geologic and weather conditions, it would be expected that element concentrations in fresh water would decline or stabilize over time as the exposed soluble crustal material was carried away. Physical disruption of water seepage channels, such as might occur during seismic dilatancy or during preseismic slip, might reasonably be expected to expose water to unleached sources of nutrient ions and the result is predictably a change in ion concentrations in fresh water flows. The crustal abundance of elements being over a factor of ten greater than their normal abundance in adjacent water enhances the probability of a measurable step in the concentration of selected ions in running water.

For example, consider potassium, whose crustal abundance is of the order of 10^4 $\mu\text{g/g}$ (about 2.6% of igneous rocks). Fresh water concentration of potassium ions is typically of the order of 10 $\mu\text{g/g}$. Exposure of such water to fresh mineral surfaces, especially under conditions of elevated pressure and temperature, could be expected to result in measurable increases in the concentration of potassium ions in the water and ultimately to measurable increases of potassium in plant material.

To summarize, nutrient elements circulate through the biosphere, largely as a result of wind and water movements. However, in the long term, volcanic and seismic phenomena account for the return of trapped or buried elements to the biosphere from layers under oceans or from desert deposits. During periods of dilatancy or preseismic slip, fresh water supplies may be exposed to unleached crustal material containing concentrations of these nutrient elements orders of magnitude greater than their concentrations in adjacent water reservoirs. Furthermore, it is possible that such exposure occurs under conditions of elevated pressure and/or temperature. The result can be a measurable increase in the concentration of nutrient elements in water flows.

Measurability of Expected Changes in Plant Material

To some extent, nutrient concentrations in plants reflect concentrations in the supplying environment. Concentration of nutrients in plants can exceed that necessary for optimal growth - "luxury consumption" - if the supplying environment contains an excess. (Epstein, p. 65) However, plants employ active ion transport mechanisms to skew the relationship between external nutrient supply and internal nutrient abundance. Very small external concentrations of vital nutrients may result in normal (to the plant) internal concentrations. (Epstein (1972)) Consequently, for nutrient elements in short supply to a plant, seismic activity may result in microscopic increases in groundwater concentrations which in turn would result in major increases in concentration in plant tissues.

In the case of elements already in relative abundance to the plant, the increase in plant tissues would be expected simply to mirror any changes in groundwater concentrations. A special case exists for competing ions (such as rubidium and potassium or bromine and chlorine) where plant active ion transport mechanisms are unable to distinguish between two ions. Plant concentrations of rubidium or bromine would normally not be high, simply because these elements are not nearly as abundant as potassium or chlorine. It would be expected that the ratio of potassium to rubidium or of chlorine to bromine in plant tissues would reflect the same ratios in the root environment. Groundwater changes in these ratios would be expected to result in similar changes in plant tissues.

Epstein (pp. 128-129) published data collected from several sources on concentrations of ions in plant root and leaf tissue. In selected plants, mainly grasses, ion concentrations in leaf tissue ranged from approximately 10^{-1} to 10^0 mM for potassium (rubidium), manganese, zinc, copper, chlorine (bromine), nitrate, phosphate, sulfate and borate. Table 2 reproduces these

results and adds a column in which the concentration is converted to nanograms per square centimeter for a sample thickness of about .25mm. The reason for this conversion is to ease comparison of Epstein's data with the next column in Table 2 - detectability limits of various key elements for 80 or 90-second analysis times in an automated x-ray fluorescence analyzer. (Jaklevic (1981))

To prevent individual sample variations from overpowering results, it will be desirable to sample rather extensively. X-ray fluorescence equipment has been in development and use for about a decade to monitor air-borne pollutants. (Goulding (1973), Jaklevic (1981)) The equipment can be used without modification to monitor elemental concentrations in leaf samples from selected vegetation in seismically active areas. Such equipment, counting 1-1/2 minutes or less per sample, can measure many leaf-carried elements at levels 10^{-2} of their expected maximum concentration. Where greater sensitivity is desired, count times can be increased.

Sample Selection and Collection

Ecological earthquake precursors are not likely to be universally measurable or useful. To increase measurability or usefulness requires care in the selection of potentially fruitful sites and in the selection of vegetation to be sampled. Sample collection areas should be free of man-made disruptions or contamination of groundwater supplies. Virgin perennial springs in relative wilderness areas would be expected to produce useable samples with the highest probability. Samples should be collected from vegetation dependent on groundwater supplies. In the Berkeley Hills, for example, good candidates are live oak trees, bay laurels and coast redwoods. Year round springs supply water to vegetation in relatively remote canyons in the area.

Another requirement is the proximity of faults. Here, again, the Berkeley Hills are central in an extensive fault system. The University of California,

in fact, supports earthquake monitoring equipment in the immediate vicinity of a perennial spring in one remote Berkeley Hills Location. (The Byerly Seismographic Station).

Development of the usefulness of ecological monitoring to earthquake prediction is a long-term project. It is first necessary to develop base-line data for extended time periods; to include seasonal change in rainfall and in other weather-related variables. If nutrient levels in plant tissues vary excessively due to non-seismic activity, it may be necessary to include weather data in the prediction activity. Nutrient levels would be expected to vary from plant-type to plant-type and perhaps even among the same type of plants in different locations. Such variables would also have to be considered in searching for seismic-produced effects. At its simplest, the project may involve simply monitoring growth on a few selected trees, looking for unusual changes in nutrient concentrations. At its most complex, a data base would need to be developed including weather data as well as topological and species-related variations of individual samples.

Probability of Success

Success or failure depends on the relative magnitudes of seismic-induced groundwater changes versus the magnitudes of such changes resulting from non-seismic phenomena. Radon level changes and isotopic anomalies of other elements in groundwater have been reported. (Wakita (1977)) Temperature changes and turbidity changes have also been noted. It is consequently not unreasonable to expect significant changes which may be detected in growing plant material.

Mineral cycling in the ecosystem has been studied extensively. (Duvigneaud (1975), Ovington (1965) and many others) Weather-related replenishment of several minerals - potassium, calcium, magnesium, nitrogen and sulphur, for

example - can be a very significant percentage of plant requirements. Such replenishment can mask the effects we are looking for. There is no guarantee that groundwater supply reservoirs will be disrupted or otherwise affected by seismic precursory activity. In short, there is no reliable way of predicting success. The only truly reliable prediction is that of failure resulting from not making the attempt.

Conclusion

The use of elemental changes in plant material as an earthquake predictor has some logical basis stemming from the combination of experiments on rock fracture and stick-slip phenomena and from empirical observations of preseismic groundwater changes. Empirical data on crustal concentrations of nutrient elements relative to their concentrations in fresh water supplies may also be used to support the possibility of using plants as precursory signal organisms. On the negative side, the small magnitude of preseismic creep, the unknown locations or dimensions of groundwater reservoirs and possible weather-related variations in nutrient availability may either mask preseismic effects or make them non-existent in many regions. Either way, the means of easily testing the possibility of using element concentrations in plant material as a preseismic predictive parameter exists today in the form of automated x-ray fluorescence analyzers.

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Element	Symbol	Atomic Wt.	Concentration in dry plant matter µg/g ⁽¹⁾	Crustal Abundance µg/g ⁽²⁾	Shale µg/g ⁽²⁾	N. American waters Lake & River ions µg/g ⁽¹⁾	Seawater µg/g ⁽²⁾
Molybdeum	M _o	95.95	.1	2	2		.01
Copper	Cu	63.54	6	60	57		.003
Zinc	Zn	65.38	20	70	80		.01
Manganese	M _n	54.94	50	1,000	850		.002
Iron	Fe	55.85	100	56,000	47,000		.01
Boron	B	10.82	20	10	100		4.6
Chlorine	Cl	35.46	100	150	160	8	19,000
Bromine	Br	79.916	()	.26	6		65
Sulphur	S	32.07	1000	260	220	20	885
Phosphorus	P	30.98	2000	1,050	770		.07
Magnesium	Mg	24.32	2000	23,000	13,400	5	1,350
Calcium	Ca	40.08	5000	41,000	25,000	21	400
Strontium	Sr	87.63	()	215	450		8.0
Potassium	K	39.10	10,000	21,000	23,000	14	380
Rubidium	Rb	85.48	()	125	270		.12

(1) Epstein, 1972 (from Epstein, 1965)

(2) Reeves and Brooks, 1978 (from various sources)

Table 1 Concentrations of nutrient elements in plants, in the earth's crust, in shale, in North America fresh water and in seawater. Seawater carried by the wind is one major source of nutrient replenishment. Another, especially in seismically active regions, may be ground water transport of minerals from various parts of the earth's crust. Elements with no value listed for concentration in dry plant matter are competitors with other nutrient elements. Rubidium may substitute for potassium, for example. Similarly, strontium may replace calcium and bromine may replace chlorine.

ION	Leaf Concentration (1) (Max., mM)	Mol. wt.	Sample Content ng/Cm ²	Detectability ngm/Cm ² XRF Analysis (2)	Ratio
K ⁺	.2 - 1.5	39.1	195.5 - 1466.25	9.14 ^a	21.4 - 160.4
R6 ⁺	.2 - 5	85.5	427.5 - 1068.75	2.8 ^b	152.7 - 381.7
Mn ²⁺	5	54.9	6862.5	13.5 ^b	508.3
Zn ²⁺	.01 - .5	65.4	1372.5 - 6862.5	5.3 ^b	259.0 - 1294.8
Cu ²⁺	.5	63.5	793.75	.5 ^b	122.1
Cl	.2	35.5	177.5	26.6 ^a	6.7
Br	.2	79.9	399.5	2.7 ^b	148.0
NO ₃ ⁻	.24	62.0	N/A	N/A	N/A
H ₂ PO ₄ ⁻	.1	97.0	77.5 (P)	32.9 ² (P)	2.4
SO ₄ ²⁻	.1	96.1	80.25	29.4 ^a (S)	2.7
H ₂ BO ₃	.2	60.1	N/A	N/A	N/A

(1) Data from Epstein (1965) pp. 128-129

(2) Data from Jaklevic and Thompson (1981)

Table 2 Maximum concentrations, their translation into XRF-analysis concentration units and minimum detectability for various plant nutrients. Boron and Nitrogen are not easily detected using automated XRF analysis because of their low atomic number. a) is for a 90-second count using a Ti secondary target. b) is for an 80-second count, Mo secondary target. XRF data from Jaklevic and Thompson, 1981. Samples are assumed to be about .025 cm thick with about 8 cm² active surface area, or .025 x 8 = .2 cm³ = .2 x 10⁻³ liters.

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