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Biogeochemistry of vanadium ...

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Abstract

Vanadium is known to occur in soils as vanadates of copper, zinc, lead, uranium, ferric iron, manganese, calcium, and potassium. Vanadium replaces aluminum in clays and occurs in porphyrin complexes in bituminous sediments.

Small amounts of vanadium are stimulating to plants; large amounts are toxic. Ten to 20 ppm vanadium in nutrient solution is commonly harmful to plants, but larger amounts can be tolerated by specific legumes, which use vanadium in the nitrogen-fixation process. Old wood in vegetation contains more vanadium than young wood, and roots contain the greatest accumulations. Herbs are more efficient accumulators of vanadium than trees and shrubs. _Allium_ and some species of _Astragalus_, _Castilleja_, and _Chrysothamnus_ are shown to be accumulators of vanadium.

The vanadium content of plants rooted in highly calcic soils is very low, and that of plants rooted in seleniferous soils is high. Outdoor plot experiments verify a decrease in the presence of selenium. The absorption and translocation of vanadium by several plant species was found to be in direct ratio to that of selenium. Plant species that absorb large amounts of calcium are most tolerant of high-vanadium soils as the vanadium is precipitated in the root.

Vanadium occurs in all animals and is accumulated in large amounts by Ascidians and by holothuroidians. Vanadium is probably essential to vertebrates. Vanadium has been shown to decrease dental caries in animals and children. Vanadium inhibits the biosynthesis of chloresterol in both animals and man. Seleniferous areas in the western conterminous United States may support vegetation that contains large amounts of vanadium. Many areas of this country on the other hand may be nutritionally deficient in vanadium.

Introduction

The association of vanadium with uranium in the sandstones of the Colorado Plateau and the search for minable deposits of both these elements has led to the collection of large amounts of information concerning the geochemistry of vanadium in sandstone and clay environments and the mobility and availability of this element in soils and plants. Because agricultural and health specialists have become interested in vanadium recently, this report summarizes available existing information on the biogeochemistry of vanadium and suggests geochemical environments in which excesses or deficiencies of this element might occur. The analyses presented in this report were made in U.S. Geological Survey laboratories by both chemical and spectrographic methods. Field collections were made in connection with research on botanical methods of prospecting.

Geochemistry

The vanadium content in plants and animals is related, logically, to the vanadium in the physical environment on which the biosphere is dependent. An average of 150 parts per million (ppm) vanadium is believed to be contained in the earth's crust (Green, 1953). This vanadium occurs in a number of valence states in a variety of materials. For instance, it occurs as a cation in a reduced form in magmatic rocks and in insoluble hydroxide minerals (Goldschmidt, 1954, p. 485); it replaces aluminum in montmorillonite clays (Foster, 1959); and it occurs as the vanadate anion in oxidized calcium, manganese, copper, zinc, lead, uranium, potassium, and ferric iron compounds. The vanadium content correlates with the organic-rich fraction of phosphate rocks (Krauskopf, 1955), the sapropelite of black organic shales, and the porphyrin complexes of bituminous sediments. The latter vanadium compounds are believed by Hodgson and others (1960) to have resulted from a reaction of vanadium salts and chlorophyl degradation products in the presence of sulfide ions shortly after deposition and burial of plant remains. As much as 43.4 percent vanadium has been reported in the ash of asphalt (Rankama and Sahama, 1950, p. 596).

In the weathering of an igneous rock in a humid climate, vanadium is incorporated in the clay minerals formed. In an arid climate it is released with aluminum hydroxide during decomposition of the clays (Rankama and Sahama, 1950, p. 599). Volcanic tuffs are robbed of their vanadium by the highly alkaline waters that are formed during devitrification (Garrels, 1957). Vanadium is thus carried in moderately reducing or strongly alkaline solutions that contain abnormal carbonate and is precipitated by oxidation in the presence of potassium or calcium by reduction or acidification chiefly in the presence of organic matter. The average content of vanadium in world soils, according to Vinogradov

(1959, p. 183), is 100 ppm. The solubility of vanadium and its availability to plants thus vary considerably in different chemical and geological environments.

Vanadium in plants

Physiological effects of vanadium on plants

The effect of vanadium on the growth of plants was first investigated before the actual presence of vanadium in higher plants had been detected. These early experiments were largely concerned with the possible toxic properties of vanadium, which occurred as a common impurity in phosphate fertilizers. From 1886 until about 1935 experiments were reported by botanists in several countries (Suzuki, 1903; Free and Trelease, 1917; Scharrer and Schropp, 1935) who agreed that small amounts of vanadium were beneficial to plants but that larger amounts were toxic. Ten to 20 ppm vanadium in solution were commonly found to be harmful to plant growth.

The physiological effects of vanadium on plant growth were reported by Warington (1956) to be a preliminary deepening of color in the shoot followed by apical iron-deficiency chlorosis. Because reddening in plants had been observed around the uranium-vanadium deposits in Utah and Colorado, Geological Survey personnel ran experiments with sorghum and *Astragalus preussi* (a selenium indicator) in nutrient solutions containing 1, 10, 100, and 1,000 ppm vanadium as ammonium metavanadate. No effect was noted in the growth of germinated seeds of sorghum at 1 ppm; reddening first of the lower stems and later of the leaf tips was noted at 10 ppm, and stunting and death occurred after 2 weeks in 100 ppm solution. The *Astragalus preussi*, on the other hand, was not affected by 100 ppm and grew 20-inch roots in 6-weeks time. Neither species grew in a solution of 1,000 ppm vanadium.

The ability of legumes to tolerate and even make use of vanadium has been noted by other workers. Arnon and Wessell (1953) working with green algae found that small quantities of vanadium gave increased growth and concluded from their experiments that vanadium probably is required by green plants. The essentiality of vanadium to plants has not been proven, however. Burk and Horner (1935) and Bortels (1936, 1937) demonstrated that at beneficial increments vanadium can replace molybdenum as a specific catalyst for nitrogen fixation. Vanadium thus is beneficial to legumes and may even be preferred over molybdenum by certain species. Two very closely related species of *Astragalus* that were being used as indicator plants in the search for uranium-vanadium deposits on the Colorado Plateau had different distribution patterns around the deposits. The difference probably is caused by the seeming preference of *Astragalus pattersoni* for molybdenum and of *Astragalus preussi* for vanadium (table 1).

The reason for these differences may be the different calcium contents of the two species, *Astragalus pattersoni* containing nearly twice as much calcium as *Astragalus preussi*. This suggests that the cell sap of *Astragalus pattersoni* has a higher pH, which would tend to precipitate the vanadium in the root but to increase the solubility and mobility of the molybdenum.

Table 1.--Differences in molybdenum and vanadium uptake by two closely related species

[Analyst, Uteana Oda]

	Average vanadium content (ppm)		Average molybdenum content (ppm)	
	In ash of plants	In soil	In ash of plants	In soil
Astragalus pattersoni (tops; 8 samples)----------------	30	260	240	8
A. preussi (tops; 10 samples)-	400	1,500	80	~7

The vanadium content varies in different parts of the plant. Samples of young and old wood of 30 shrubs collected on the Phosphoria Formation in Wyoming contained twice as much vanadium in the older parts of the plant as in the younger (Fred Lotspeich, written communication, 1960). Thirteen coniferous species averaged 29 ppm vanadium in the needles; 47 ppm in the twigs; >100 ppm in the roots. The only cone sample contained 112 ppm. By far the greatest concentration of vanadium in a plant occurs in the root. Thirty-five near-surface juniper roots collected in the Thompson uranium-vanadium district in Utah averaged 110 ppm vanadium in the ash and the branch tips of the same trees averaged only 55 ppm. A peeled juniper root collected from the ore zone at a depth of 9 feet contained 2,200 ppm vanadium; the same root near the surface only 78 ppm.

Analyses of Colorado Plateau plants suggest that the vanadium content of plants rises during the growing season and that larger amounts of vanadium are absorbed by herbs than by trees and shrubs (table 2).

Table 2.--Vanadium in the ash of plants from mineralized and unmineralized parts of the Thompson district, Grand County, Utah

[Analysts: Uteana Oda and H. E. Crowe]

	Vanadium (ppm)		Ratio mineralized/unmineralized
	On mineralized ground	On unmineralized ground	
Grasses----	135	25.	5.4
Other herbs including selenium indicators-----	191	35.6	5.4
Trees and shrubs---	51	19.8	2.6

Vanadium absorption by plants

The absorption of vanadium by plants is dependent upon the amount of available or water-soluble vanadium in the soil. In the zone of oxidation this amphoteric element forms compounds with calcium, ferric iron, and potassium. It is also easily incorporated into the lattice of clays. The contents of vanadium absorbed and translocated to the above-ground parts of various classes of vegetation, which have been averaged from all available analyses, are shown in table 3. The lower forms of plants contain more vanadium than seed-producing plants. The largest amounts of vanadium have been reported in a poisonous mushroom *Amanita muscaria*, which contained 112 ppm vanadium in the dry weight, or about 1,900 ppm in the ash (Bertrand, 1943a). Collections from various parts of France indicate that the species is a universal accumulator of vanadium.

The concentrations of vanadium in some species that grow around uranium-vanadium deposits in the west are very high, as shown in table 4.

The vanadium contents shown are noteworthy when compared to the average contents shown in table 3 or to 1 ppm dry weight or 7.1 ppm in the ash reported by Bertrand (1950).

Table 3.--Average contents of vanadium in the ash of various classes of vegetation rooted in unmineralized soil

[Averaged from published analyses and analyses in U.S. Geological Survey files]

Types of vegetation	Number of analyses	Vanadium (ppm)	
		In ash	In dry weight
Grasses------------------------	27	20	1.4
Legumes------------------------	60	12	.84
Forbs (other than legumes)------	41	20	1.20
Deciduous shrubs---------------	76	30	2.7
Deciduous trees----------------	32	15	1.65
Conifers-----------------------	85	21	.69
Equisetum----------------------	32	14	2.4
Ferns--------------------------	6	20	1.28
Fungi--------------------------	327	7	.22
Mosses-------------------------	5	200	108.
Lichens------------------------	11	98	8.6

Table 4.--Vanadium accumulator plants of the Thompson district, Grand County, Utah

Species	Average vanadium content (ppm)	
	In ash	In dry weight
Allium macropetalum (root)	700	133
Astragalus confertiflorus	900	144
A. preussi	560	67
Castilleja angustifolia	100	22
Chrysothamnus viscidiflorus	139	37
Cowania stansburiana	185	7.4
Eriogonum inflatum	125	15
Gutierrezia divaricata	155	9.3
Oryzopsis hymenoides	165	10

The absorption from carnotite [$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$] is compared in figure 1 with that from other types of deposits. The normal ratio of vanadium in the soil to that in the plant ash is about 10 to 1. From those rocks that contain a large amount of calcium, like the tyuyamunite [$Ca(UO_2)_2(VO_4)_2 \cdot nH_2O$] deposits at Grants, N. Mex., and from sandstones with calcium cement, plant absorption of vanadium is low; on sandstones and shales that support seleniferous vegetation the plant absorption is high. Vanadium also appeared to be unusually available in samples of river alluvium collected in several drainages of New Mexico.

Plot experiments

Plot experiments were set up in a desert environment in order to study the effects of carnotite ore and its toxic components, uranium, vanadium, and selenium, on plant life. In the plots to which carnotite had been added, plant growth was stimulated rather than retarded; less than 6 ppm of the total 600 ppm vanadium was found to be water soluble. Analyses of four species that were grown to maturity in all carnotite plots and in the control plot to which nothing was added are shown in table 5. No consistent relations between the absorption of vanadium and the pH of the soil was found. The contents of vanadium in the above-ground parts of the plants were depressed by $CaSO_4$, $CaCO_3$, and also $Ca_3(PO_4)_2$ but were generally increased in plots containing selenium. Similarly selenium uptake was increased in the presence of carnotite. These data will be reported in a later paper. The ratio of vanadium found in the roots to that in the tops when the plants were eventually harvested was found to be greater in calcium plots, as shown in table 6.

As the water-soluble vanadium in the soils of all of these plots was less than 6 ppm the amounts of vanadium accumulated in the roots are rather remarkable. The data suggest that the vanadium is probably precipitated as calcium vanadate within the root. Astragalus preussi, a vanadium accumulator, was able to extract as much vanadium from the selenium plot where no vanadium had been added as the Grindelia extracted from the carnotite plot (table 6).

The contents of vanadium in ash have been plotted (fig. 2) against selenium, sulfur, calcium, and phosphorus contents from samples of Grindelia and Descurainia that were grown in the carnotite plots. A direct correlation exists between the contents of vanadium and selenium that are absorbed and translocated to the above-ground parts of these plants but no correlation exists with any other element.

Vanadium contents of these plants were also plotted against total contents of certain elements in the soil as shown in figure 3. No relationship was found between vanadium absorption and the contents of iron or sodium in the soil but an apparent inverse relationship exists with calcium and uranium. The depressing effect of uranium on vanadium absorption is surprisingly strong considering that vanadium and uranium were added together as carnotite and hence total amounts in the soil were in direct ratio. Two few soil analyses were available to plot sulfur, selenium or phosphorus.

In the plots to which sodium vanadate was added, 840 ppm of vanadium was found to be water soluble after a few weeks time and no planted species were able to grow in the plots during the first season. An interesting volunteer, an unidentified species of Amanita, appeared in two vanadium plots and in the control plot. Growth of this mushroom was stimulated by the vanadium; the sample collected from the control plot contained <15 ppm; that from the vanadium-lime plot, 200 ppm.

Table 5.--Vanadium in ash of above-ground parts of experimental plants

[In parts per million. Soils of each plot contained <6 ppm water soluble vanadium. Analysts, Uteana Oda and H. E. Crowe]

Plant and year	Control	Carnotite $[K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O]$	Carnotite + $CaSO_4 \cdot nH_2O$	Carnotite + $CaCO_3$	Carnotite + $Ca_3(PO_4)_2$	Carnotite + Na_2SeO_3
Grindelia						
aphanactis, 1954----------	50	105	25	15	25	84
Descurainia obtusa, 1954----	<15	100	24	------------	20	250
Eschscholtzia						
californica, 1954---------	<15	<15	30	<15	<15	75
Verbesina						
encelioides, 1954---------	10	25	<15	<15	10	20
pH of soil-----------------	6.6	7.3	7.0	6.9	6.5	7.7

Table 6.--A comparison between vanadium in ash of tops and roots of experimental plants

[Analysts, Uteana Oda and H. E. Crowe]

Plant and year	Plot	pH	Tops (vanadium, ppm)	Roots (vanadium, ppm)	Vanadium content ratio roots/tops
Verbesina, 1955	Carnotite plus calcium phosphate	7.5	10	1,500	150
Grindelia, 1955	Carnotite plus gypsum	7.7	35	500	14
G., 1956	Carnotite	6.7	50	150	3
Astragalus preussi, 1956	Sodium selenite	7.9	50	150	3

By the second year, after a winter of leaching, four species of plants were grown and harvested from soils containing the contents of water-soluble vanadium shown in table 7. Toxicity symptoms were extreme dwarfing and chlorosis. The remarkable ability of these plants to reject vanadium or at least to prevent the translocation to the leaves, stems, and fruits is most interesting. Verbesina, able to grow in the most vanadiferous soil solution, contained the least vanadium in the above-ground portion of the plant. All four species contained large amounts of calcium and it is probably because of this tendency that the species were able to grow in highly vanadiferous soils. In experiments run by Krioukov (1931) with sodium vanadate, 22 ppm vanadium in the soil caused an 80 percent diminution of oat crops and 66 ppm vanadium completely halted oats and mustard.

Table 7.--Plant tolerances to sodium vanadate noted in plot experiments

[Analyst, Uteana Oda]

Plant harvested	Vanadium in plant ash (ppm)	Water-soluble vanadium in soil (ppm)
Grindelia aphanactis------	150	140
Cleome serrulata----------	80	280
Descurainia obtusa--------	80	560
Verbesina encelioides-----	40	560

Vanadium in animals

Vanadium has been found in the tissues of representative species from all the animal phyla (Bertrand, 1943a). For invertebrates excluding Ascidians, the amounts found were of the order of 1.2 ppm vanadium in the dry matter; for vertebrates about 0.1 ppm. Vanadium is known to be concentrated in certain groups of Ascidians or sea squirts (Bertrand, 1943b) in amounts averaging 40 ppm dry weight. Henze, Stöhr, and Müller (1932) have shown that the chromogen does not function as an oxygen carrier in the blood but on the contrary acts as a powerful reducing agent to effect a synthesis of carbohydrate from CO_2. A holothuroid, or sea cucumber, was also found to accumulate vanadium, containing 1,235 ppm vanadium in the dry weight (Phillips, 1918).

Experiments have shown that concentrations of 5-6 ppm vanadium are toxic to rabbits (Ballota, 1931), and of 4-5 ppm as $NaVO_3$ to rats (Franke and Moxon, 1936). Vanadium is important in normal calcium metabolism of osseous tissues; carious teeth develop in vanadium-deficient animals (Rygh, 1949). Caries can be prevented in hamsters by the addition of 0.08 mg V_2O_5 once a week to the diet (Geyer, 1953). Studies of children were carried on by Tauk and Storvick (1960) in an area in which the vanadium content in the water ranged from 0.03-0.22 ppm. A decrease in dental caries was found to correlate with an increase in vanadium.

Lewis (1959) has shown that workers in vanadium mines of southwest Colorado have significantly lower cholesterol content than control groups. Vanadium has also been shown to reduce the excess cholesterol in the rabbit aorta (Curran and Costello, 1956) and to reduce phospholipid content of rabbit livers (Mountain, Stockell, and Stokinger, 1956). They conclude, therefore, that vanadium may be a factor in the prevention or cause of heart disease.

Geologic effect on availability and its relation to health

The meager data that exist on vanadium in the biosphere thus suggest that vanadium absorption by plants may be deterred by the presence of calcium in the soil and that the tops of calcium-loving plants will contain less vanadium in a given environment than other plants although the roots may have large concentrations. The data also suggest either that vanadium uptake is enhanced by the presence of selenium or that the absorption of the two elements is favored by the same soil environment. In either event, plants in areas of selenium toxicity may be high in vanadium. By contrast, above-ground crops rooted in high-calcium soils may be so deficient in vanadium as to affect animal nutrition, although the root crops grown in the same soils may be nearly toxic. The known vanadium content of vegetation in different parts of the country have been plotted on a map of the conterminous United States in figure 4. The highest vanadium values occur in the seleniferous areas of the country as shown. Great areas of deficiency may also exist. Little is known and much remains to be learned about the ecology and distribution of this interesting element.

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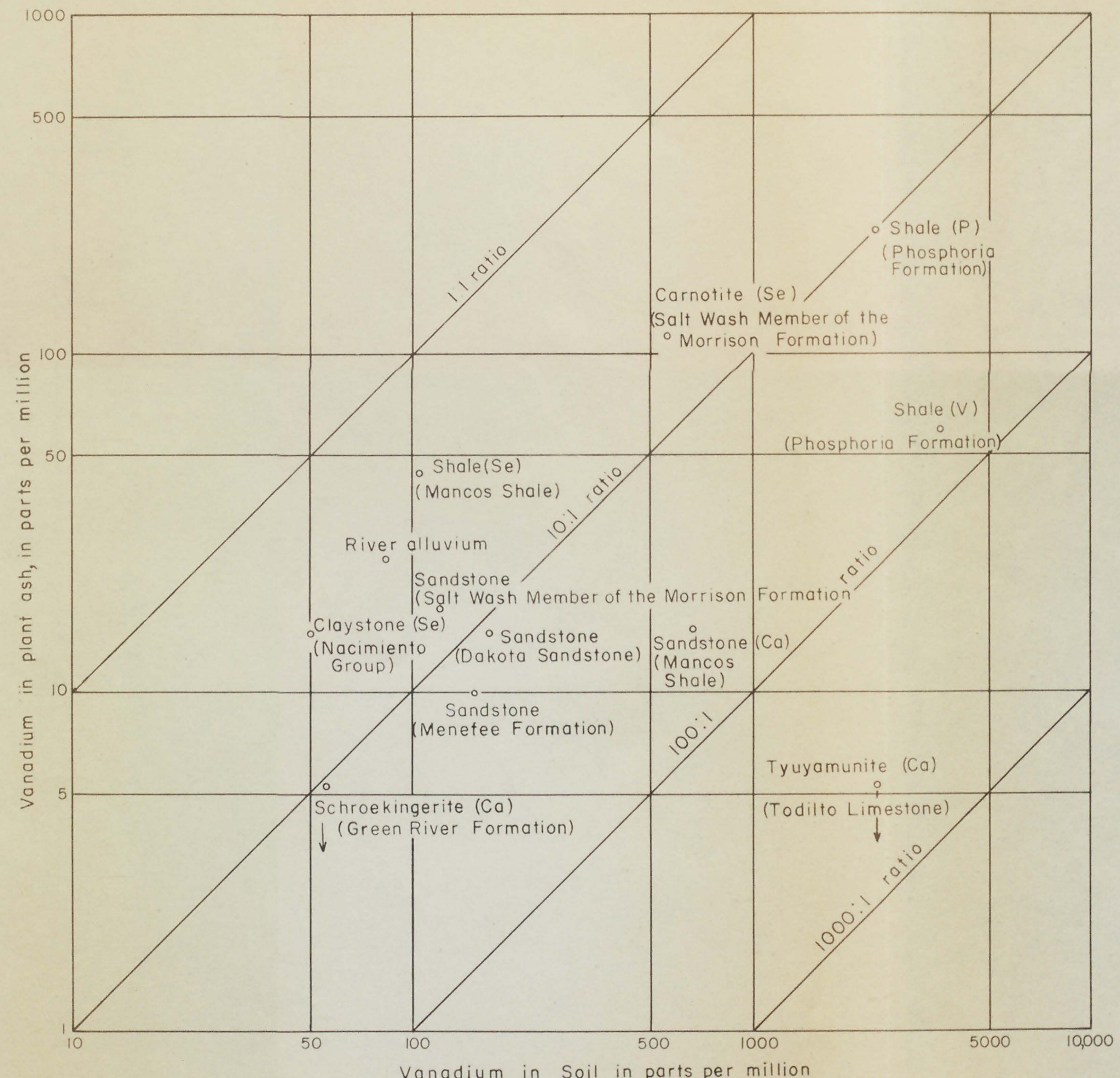

Figure 1.– Absorbtion of vanadium by plants rooted in different chemical environments

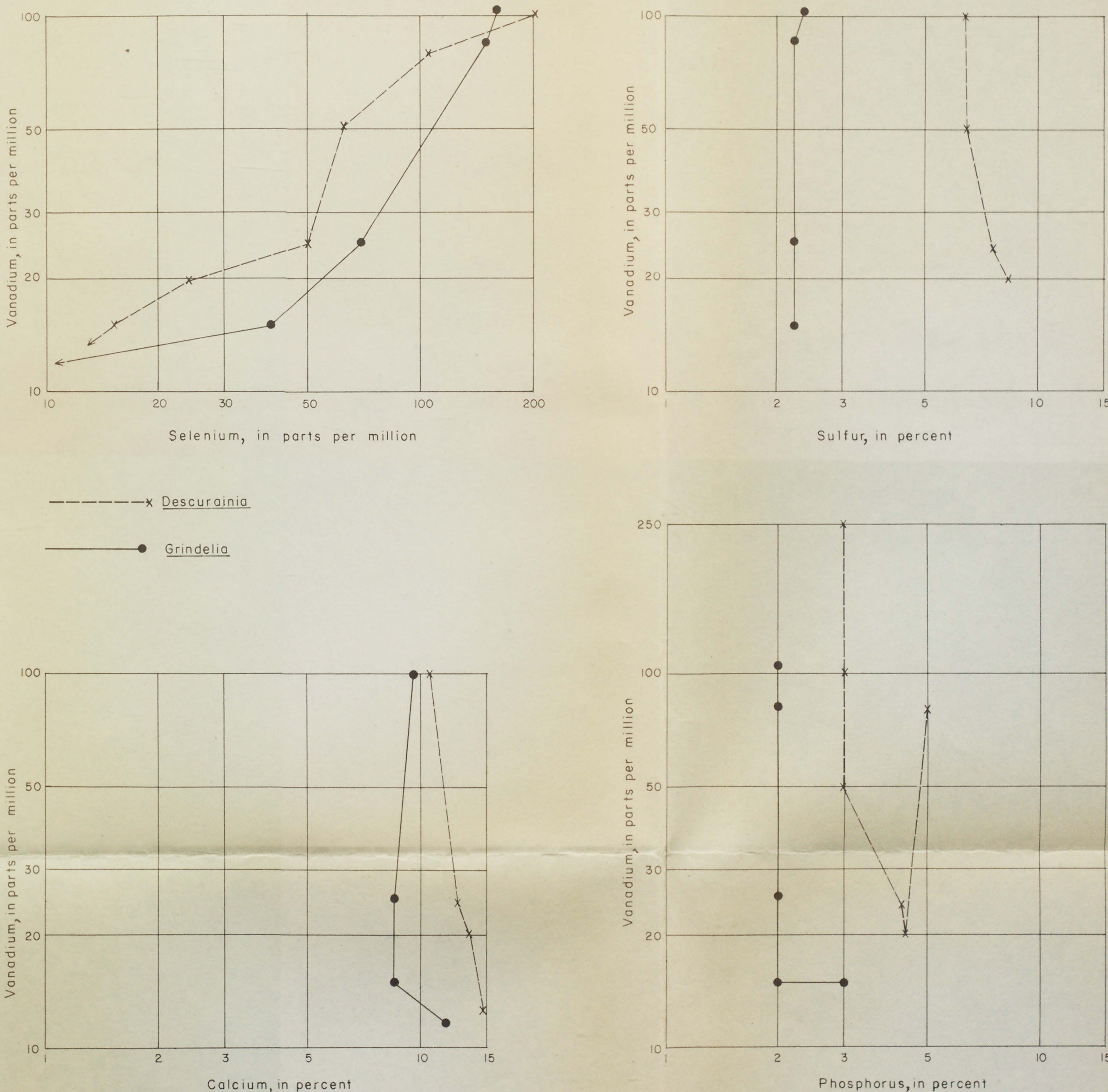

Figure 2.– Absorption of V compared to that of Se, S, Ca, and P in above-ground samples of Descurainia and Grindelia grown in plot experiments

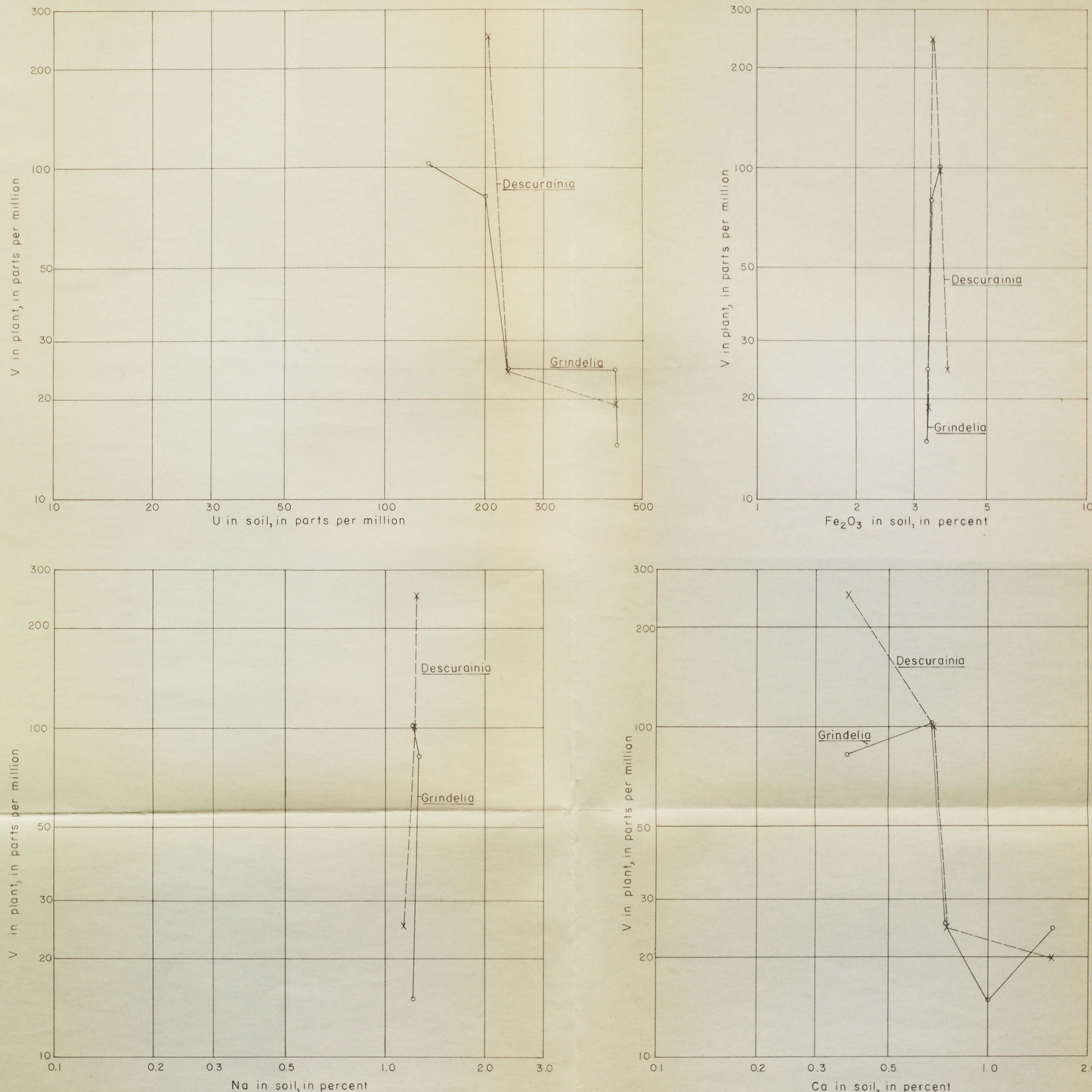

Figure 3.– Absorption of vanadium by Descurainia and Grindelia from soils of varying uranium, ferric oxide, sodium, and calcium content

Figure 4. Vanadium content of vegetation in the conterminous United States