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Geochemical Assessment of Iron and Vanadium Relationships in Oxic Soil Environments

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Geochemical assessment has become a cost-effective and highly accurate tool for estimating metal contamination, especially in those cases where the level of contamination is not considered severe. Difficulties frequently arise in attempting to discriminate between pristine metal concentrations and low-level environmental impacts. As an example, Vanadium contamination is frequently associated with coal and petroleum bi-products; however, air and water contamination pathways are also possible. The purpose of this investigation was to characterize the V and Fe concentration relationship among a wide variety of soil types and to formulate an estimate of the pristine V concentrations in these soils. If a linear relationship may be established between Fe and V, then geochemical analysis of impacted soils may discriminate between V as a natural background component and anthropogenic V. Forty-six moderately well-drained to well-drained soil profiles having cambic, argillic or calcic soil horizons were characterized for Fe and V using an aqua-regia digestion to determine if these soils exhibited a one-to-one correspondence between V and Fe. Such a correspondence was authenticated for the majority of these soils and may be used to discriminate between natural and anthropogenic V. The presence of argillic, calcic or fragipan horizons did not reduce the one-to-one correspondence between V and Fe, suggesting that these soil processes did not selectively partition either V or Fe. The method needs to be further evaluated for soils having anoxic soil conditions, lithologic discontinuities and other specific pedogenic processes.

Keywords Vanadium, iron, soils, vanadyl, pervanadyl

Total elemental analysis was a common tool in the early development of both soil science and geochemical prospecting, but the development of selective extractions and other experimental techniques revealed that elements reside in an array of soil environments, which influences their unique chemistry and bioavailability (Shuman, 1991). Chemical instrumentation advancements have allowed the rapid and low-cost estimation of element abundances, particularly important when coupled with selective soil extractions.

Metal Assessment and Environmental Quality

The onset of any environmental study involving metal contamination involves the selection of an experimental protocol and the criteria for data analysis. Single-step extractions are frequently used because of the simplicity, low-cost, and relative ease of data interpretation, whereas selective-sequential extractions offer a better estimate of the soil/sediment chemistry resulting in the partitioning of metals into chemically defined soil environments

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(Shuman, 1991). Selective-sequential extractions also generally provide more insight into the biological availability and potential fate and transport potentialities of metals. Difficulties associated with selective-sequential extractions include: (1) the lack of commercial laboratories to perform many of the documented extractions, and (2) the lack of standardization of many of these extractions, such that compliance personnel have difficulty selecting the appropriate protocol.

Data analysis may be referenced relative to: (1) crustal materials or specific earth-material averages, (2) on-site pristine materials, or (3) an internal constituent, such as an element (Fe, Ti, Zr), clay content, or a specific mineral. Rule (1986) recommended that environmental geochemical data should utilize mean concentrations, cumulative frequency plots, and metal/Fe ratios, particularly when pristine samples are unavailable. Similarly, Herut *et al.* (1993) documented the trace metal concentrations of Hg, Pb, Cu, Zn and Cd indexes relative to Fe for marine sediments along the coast of Israel. They observed that trace metal variations were attributed to the mixing of sediments having variable trace and Fe contents and both point and non-point influences.

Vanadium

Vanadium (V) contamination of soil may occur whenever petroleum or coal bi-products are accidentally discharged (Kabata-Pendias and Pendias, 1985). Other potential sources of contamination include phosphate fertilizers and mining activities, particularly the mining of phosphate and uranium. Soils from parent material classes featured in this manuscript typically have the following V abundance ranges: sandstone and limestone derived soils (10 to 91 mg V × kg^{-1}), shales and argillaceous sediments (20 to 150 mg V × kg^{-1}) and loess (27–110 to mg V × kg^{-1}) (Kabata-Pendias and Pendias, 1985).

Vanadium (V) is the 23rd element in the periodic table, having an [Ar] $3d^3 4s^2$ electronic configuration (Lee, 1992). Vanadium maintains four oxidation states: +2, +3, +4 and +5, with V^{2+} unstable in the soil environment ($V^{3+} + e^- = V^{2+}$; $E^o = -0.245$ volts). The V^{3+} state is frequently a lattice component of selected primary minerals (Hurlbut and Klein, 1977) and the V^{3+} ion is considered stable only in acid and strongly anoxic soil environments (Baes and Mesmer, 1976). The vanadyl ion (VO^{2+}), having a 4+ oxidation state, exists primarily as a tetragonal bipyramid species, ideally represented as $VO(H_2O)_5^{2+}$ (Baes and Mesmer, 1976). Reduction of the vanadyl ion may be written as:

$$VO^{2+} + 2H^+ + e^- = V^{3+} + H_2O; \quad E^o = 0.359 \text{ volts}$$

The pervanadyl ion (VO_2^+), having a 5+ oxidation state, exists only in very oxic soil environments. At V concentrations normally expected in soil environments, the vanadyl and pervanadyl ions are electroactive pairs, particularly in acidic soil environments (Lee, 1992):

$$VO_2^+ + 2H^+ + e^- = H_2O + VO^{2+}; E^o = 1.00 \text{ volts.}$$

Under normal soil conditions, the conversion of the pervanadyl ion to the vanadyl ion occurs near the Eh-pH boundary separating the aerobic and moderately reduced soil environments.

Both the vanadyl and pervanadyl ions have extensive hydrolysis chemistries, involving dimer and higher ordered polymer species at concentrations exceeding 2×10^{-2} mole V/liter. Hydrolytic products of the vanadyl ion include: $VO(OH)^+$ (log K = −5.67) and $VO_2(OH)_2^{2+}$ (log K = −6.67). The hydrolyic products of the pervanadyl ion include: $VO(OH)_3$ (log K = −3.2), $VO_2(OH)_2^-$ (log K = −7.0), $VO_3(OH)^{2-}$ (log K = −7.8) and VO_4^{3-} (log K = −14.26). The $VO_3(OH)^{2-}$ species is important in soils having a moderately alkaline pH, typically soils that are dominated by Ca-carbonate (pH 8.3). The VO_4^{3-} species is only important in excessively alkaline soils ($pH > 12$).

Vanadium substitutes for P and As (Hurlbut and Klein, 1977), because the ionic radii of P, As and V permit the formation of similarly sized tetrahedral units (PO_4^{3-}, AsO_4^{3-}, VO_4^{3-}). Although a variety of minerals may contain V, the weathering of apatite and Fe-bearing primary minerals may release substantial amounts of V to the soil environment. Typical vanadium containing minerals include Carnotite $K_2(UO_2)_2(VO_4)_2 \cong 3H_2O$ and Vanadinite $Pb_5(VO_4)_3Cl$ (Hurlbut and Klein, 1977).

Gehring *et al.* (1993) demonstrated that VO^{2+} occupied substituted sites in layer silicates, especially mica minerals. Schwertmann and Pfab (1996) proposed that V^{3+} was present in Fe-rich lateritic profile from northern Sudan. They also proposed that coodinative stabilization of structurally incorporated V^{3+} inhibited Fe reduction and V^{3+} oxidation, fostering the long-term stability of V-bearing goethite.

Fox and Doner (2002) showed that V accumulated on goethite-coated sand in a constructed wetland. Iron oxides are amphoteric surfaces and the sorption of $VO_2(OH)_2^-$ is particularly feasible in acidic soil environments, whereas VO^{2+} and $VO(OH)^+$ adsorption would be feasible in either alkaline environments or soils containing Mn-oxides (Essington, 2004). Other possible important V pathways include: (1) organic complexation and leaching, and (2) plant uptake. The potential pathways for V are illustrated in Figure 1.

Iron

Iron is the 26th element of the Periodic Table, having an electronic configuration of [Ar] $3d^6 4s^2$. Iron is an exceptionally abundant element, possessing 2+ and 3+ oxidation states in octahedral coordination in a variety of primary and secondary minerals. The soil chemistry of Fe h as been extensively reviewed (Baes and Mesmer, 1976; Langmuir, 1997; Sparks, 1999; Stuum and Morgan, 1996; Essington, 2004).

The ability of Fe to participate in oxidation-reduction reactions across a wide range of pH and Eh soil environments may be written as:

$$Fe^{3+} + e^- = Fe^{2+}; \qquad E^o = 0.770 \text{ volts},$$

$$Fe(OH)_1^{2+} + H^+ + e^- = Fe^{2+} + H_2O; \quad E^o = 0.899 \text{ volts},$$

where Fe^{3+}—hydroxy coordination influences the reduction potential and allows acidic soil environments to easily maintain the Fe^{2+} activity (Langmuir, 1997).

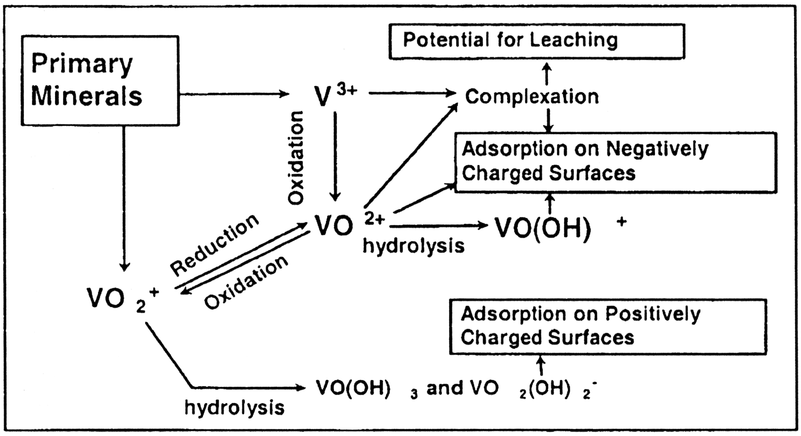

Figure 1. Illustration of the vanadium pathways and source-sink relationships in soil.

Soil Processes and Vanadium Partitioning

Positive and linear correlations of Fe and V in the soil environment are frequently observed (Kabata-Pendias and Pendias, 1985). Soils developed in similar parent materials are likely to reflect the same overall Fe-V relationship as the parent material, unless soil processes act to selectively partition V with respect to Fe. Soil processes likely to promote the preferential accumulation of V with respect to Fe include: (1) soil organic matter complexation coupled with organo-metallic illuviation, (2) oxidation-reduction processes, (3) adsorption/precipitation reactions, possibly coupled with lessivage (preferential clay migration in the soil profile), and (4) discrete changes in the parent material assemblages.

The complexation of V with soil organic matter is feasible given the array of carboxylic acid and amine functional groups present in soil organic matter (Essington, 2004) and the well-documented podzolization processes involving eluvial-illuviation of metal-organic complexes (Buol *et al.*, 2003). Argillic horizon formation involves the preferential accumulation of clay attributed to aggregate dispersion in the eluvial soil horizons coupled with the slow downward migration of the clay particles and their accumulation in the illuvial soil horizons (Buol *et al.*, 2003). It is well-documented that Fe-oxides may preferentially accumulate in the clay fraction (Aide *et al.*, 2002; Aide *et al.*, 2004) and the specter of Fe-clay co-illuviation exists. The relative intensity of V to participate in the Fe-oxide-clay complex strongly influences the extent that V may be negatively or positively partitioned between albic and argillic soil horizons.

Clearly, discrete parent materials differences provide an inheritance factor involving different V and Fe relationships, such that any initial V or Fe concentration gradient throughout the soil profile may obscure the relationships between V and Fe in the soil.

The purpose of this investigation is to assess Fe and V concentrations in a series of soils having cambic, argillic and calcic diagnostic soil horizons and to determine if these pedogenic horizons promote the preferential movement of V with respect to Fe. In the absence of any preferential partitioning of V with respect to Fe and the confirmation that the V concentrations are predictably related to those of Fe, then a simple and cost-effective method to discriminate between background and anthropogenic V concentrations based on the soil's Fe-V relationship is possible.

Materials and Methods

Soils

Fourty-six pedons were selected from four soil orders: Alfisols, Aridisols, Entisols and Ultisols (Table 1). These pedons represent a wide variety of geologic materials: (1) coastal plain, (2) loess, (3) rhyolite and rhyodacite residuum, (4) limestone residuum and (5) shale and represent biomes located in Missouri, Mississippi, Texas and Wyoming (Table 2). With the exception of the Wyoming soils, each of these soils has been the subject of previous investigations, which document their physical, chemical and mineralogical properties (Aide and Aide, 2003; Aide and Smith-Aide, 2003; Aide and Marshaus, 2002; Aide *et al.*, 2002; Aide and Smith, 2001; Aide *et al.*, 1999; Aide *et al.*, 2004).

Laboratory Analysis

Samples were air-dried and sieved to remove fragments greater than 2 mm. Particle size separation involving the Escambia, Irvington, Scholten and Goss pedons was performed using

Table 1
Soils selected to assess Fe and V relationships

Series	Classification	Drainage	Horizon sequence
Escambia	Coarse-loamy, siliceous, semiactive, thermic Plinthaquic Paleudults	Moderately well	A, E, Bt, Btvx
Goss	Clayey-skeletal, mixed, active, mesic Typic Paleudalfs	Well	A, 2Bt
Hildebrecht	Fine-silty, mixed, mesic Typic Fragiudalfs	Moderately well	A, E, Bt, Bx, 2Bt
Irvington	Fine-loamy, siliceous, semiactive, thermic Plinthic Fragiudults	Moderately well	A, E, Bt, Btvx
Jonca	Fine-loamy, mixed, active, mesic Oxyaquic Fragiudalfs	Moderately well	A, E, Bt, Bx
Knobtop	Fine-silty, mixed, active, mesic Aquic Hapludults	Moderately well	A, E, Bt, 2BC
Lajitas	Loamy-skeletal, mixed, superactive, nonacid, thermic Lithic Torriorthents	Well	A
Menfro	Fine-silty, mixed, active, mesic Typic Hapludalf	Well	A, E, Bt, C
Scholten	Loamy-skeletal, siliceous, active, mesic Typic Fragiudalfs	Moderately well	A, E, Bt, Btx, 2Bt
Taumsauk	Loamy-skeletal, mixed, active, mesic Lithic Hapludults	Well	A, E, Bt
Unnamed	Coarse-loamy, mixed, semiactive, mesic Typic Hapludults	Well	A, E, Bt

Wind River Basin Soils: Well drained soils developed in sodic shales and sandstone or alluvium derived from sodic shales and sandstone from the Wind River Basin in central Wyoming, soils include Haplocambids (5 soils), Haploargids (2 soils), Calciargids (2 soils), Haplocalcid (1 soil), Torriorthents (2 soils), Natrargids (1 soil).

Na-saturation of the exchange complex, washing with water-methanol mixtures, dispersion in Na_2CO_3(pH 9.2) and centrifuge fractionation and wet sieving (Carter, 1993).

An aqua-regia digestion (AR) was assayed for the near total concentrations of Fe and V with analytical determination of Fe and V using inductively coupled plasma-emission spectroscopy (ICP-OES). AR is a semi-selective digestion used to estimate elemental abundances associated with an extensive array of soil environments, including the nearly complete recovery of the soluble, exchangeable, organic, oxyhydroxide fractions and the limited recovery of the phyllosilicate and calcic feldspar fractions (Aide *et al.*, 2002).The AR digestions and elemental analysis (ICP-OES) were performed by SGS Laboratories (Toronto, Ontario), using the method in Van Loon and Barefoot (1989). SGS laboratories routinely uses reference samples and sample duplicates to guarantee analytical quality.

Data Presentation

Iron concentrations (g-Fe × kg-soil^{-1}) are presented as the independent variable and the vanadium concentrations (mg-V × kg-soil^{-1}) are presented as the dependent variable using linear regression analysis (Neter and Wasserman, 1974). In all cases, the linear regression

Table 2
Descriptions of selected attributes to describe the soils selected to assess relationships among Fe and V

Series	State	# Pedons	Parent materials	Biomes
Escambia	Mississippi	2	Coastal plain	Temperate forest—subtropical
Goss	Missouri	1	Thin loess/limestone residuum	Temperate forest
Hildebrecht	Missouri	2	Thin loess/limestone residuum	Temperate forest
Irvington	Mississippi	2	Coastal plain	Temperate forest—subtropical
Jonca	Missouri	2	Thin loess/sandstone residuum	Temperate forest
Knobtop	Missouri	3	Rhyolite	Temperate forest
Lajitas	Texas	12	Rhyolite	Desert, semi-arid
Menfro	Missouri	3	Loess	Temperate forest
Scholten	Missouri	2	Thin loess/limestone residuum	Temperate forest
Taumsauk	Missouri	2	Rhyolite	Temperate forest
Unnamed (Udults)	Missouri	2	Rhyodacite	Temperate forest
Wind River Basin	Wyoming	13	Holocene alluvium	Grassland, cool

was described as $y = \beta_o + \beta_1 x$, where β_1 was tested for statistical significance ($\beta_1 = 0$) using the t-statistic at $p = 0.05$.

Results

Shallow Soils Developed on Igneous Rock in a Semi-Arid Climate

The Lajitas (Lithic Torriorthents) series are soils developed from rhyolite residuum in the Chisos Mountains of southernmost Texas. The Lajitas series consists of very shallow soils containing only an A horizon, thus each sample represents a somewhat different chemical expression of the underlying igneous formation. Vanadium does not exhibit a significant linear relationship with Fe, a feature attributed to the very small range in the V and Fe values of both the igneous parent material and the soil (Table 3). Thus, the compositional homogeneity of the parent material and soil resists any development of a linear relationship involving Fe and V; however, the compositional uniformity of the soil would likely guarantee that any soil V contamination could be easily isolated using t-statistic mean separation.

The Wind River Basin Soils

Thirteen well-drained pedons resting on either sodic shale or alluvium derived from sodic shale represent the following great groups: Haplocambids, Haploargids, Calciargids, Haplocalcids, Torriorthents and Natrargids. When pooled, these soils demonstrate very strong and positive linear correlations involving Fe-V (Figure 2). Strong correlations among many pedons derived from a common parent material, but differing in topographic position,

Table 3
Soil iron and vanadium relationships for selected soils

Series	Range in Fe concentration g-Fe × kg^{-1}		Range in V concentration mg-V × kg^{-1}		V vs Fe r^2	β_1	β_0
Escambia	3	125	3	80	0.82	0.65	9.22
Goss	8	56	10	150	0.95	2.69	−6.46
Hildebrecht	7	26	12	45	0.91	1.49	3.23
Irvington	3	100	3	340	0.96	3.01	−5.66
Jonca	8	27	16	44	0.99	1.43	4.95
Knobtop and Taumsauk	16	51	10	65	0.85	1.04	6.65
Lajitas	16	22	12	22	-NS-	—	—
Menfro	12	24	18	32	0.99	1.06	7.67
Scholten	7	60	16	140	0.99	2.18	−6.58
Unnamed (Hapludults)	10	45	14	66	0.96	1.27	1.48
Wind River Basin	7	21	8	28	0.91	1.42	−1.06

-NS- = Not significant.

and having differences attributed to the presence of argillic and calcic horizons do not appreciably discriminate between Fe and V. Thus, at least for this suite of soils, pedogenic processes responsible for argillic and calcic soil horizon formation did not selectively partition V with respect to Fe.

Soils Developed in Loess Over Rhyolite and Rhyodacite Residuum

The moderately well-drained Knobtop (Aquic Hapludults) and the well-drained Taumsauk (Lithic Hapludults) pedons were developed in a solum-thick loess mantle incorporated with rhyolite residuum, whereas the well-drained Typic Hapludult pedons (series not yet

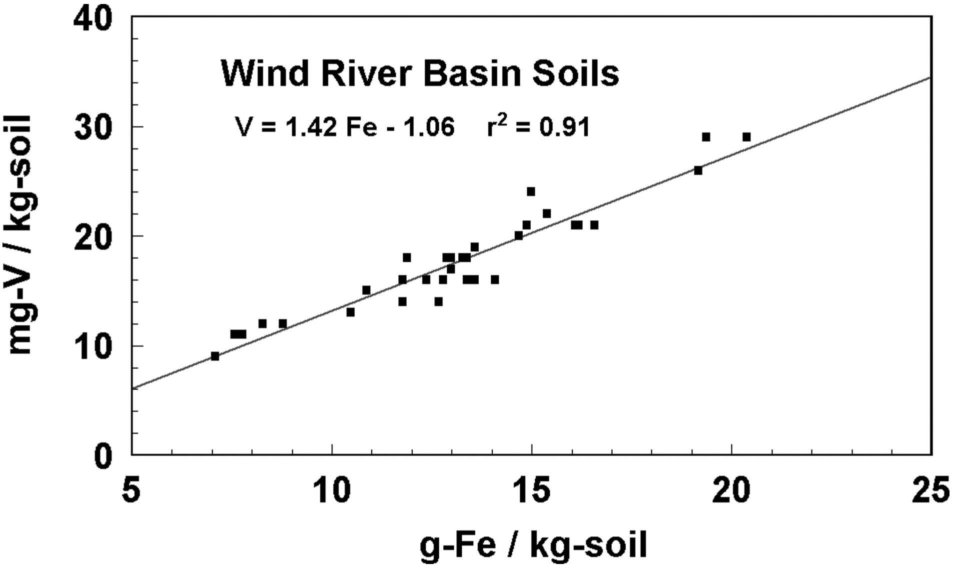

Figure 2. Iron and V relationships for soils located on sodic shale in Wyoming.

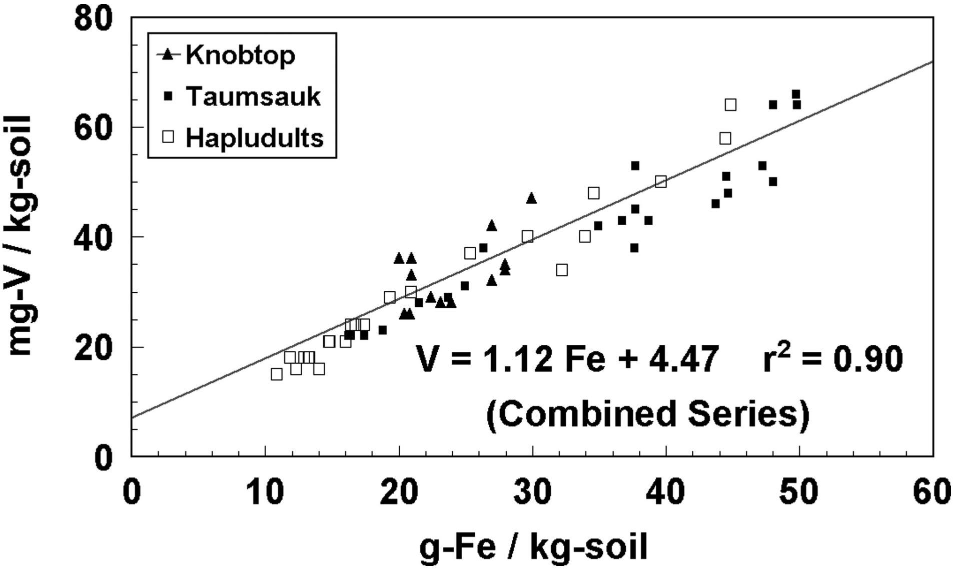

Figure 3. Iron and V relationships for soils developed on rhyolite and rhyodacite in Missouri.

established by Natural Resources Conservation Service) were developed in a thin loess mantle resting on rhyodacite residuum (Aide *et al.*, 1999; Aide and Aide, 2003). All pedons were located in the St. Francois Mountains in Missouri.

Vanadium and Fe show a strong linear correspondence among the pooled Knobtop and Taumsauk pedons ($r^2 = 0.85$) and also between the pooled Typic Hapludult pedons ($r^2 = 0.96$) (Table 3), suggesting that argillic horizon formation and landscape position did not discriminate between V and Fe. The β_1 values from the three Ultisol series were sufficiently similar that pedon pooling maintained a significant Fe-V relationship, even in the presence of somewhat contrasting parent materials (Figure 3). Argillic horizon formation, soil acidification and substantial cation leaching processes in these Ultisols did not promote sufficient partitioning of V, relative to Fe, to develop soil horizons with detectable zones of V-accumulation or V-depletion.

Plinthite-Bearing Coastal Plain Soils

The Escambia pedons (Plinthaquic Paleudults) and Irvington pedons (Plinthic Fragiudults) developed in highly weathered coastal plain materials and contain Btvx (plinthite-brearing) soil horizons (Aide *et al.*, 2004). Plinthite is an iron-rich, humus-poor mixture of clay with fine quartz and other diluents that change irreversibly to an ironstone hardpan or aggregate on exposure to sunlight (Buol *et al.*, 2003).

Vanadium concentrations show a linear correspondence with Fe concentrations in these plinthite-bearing soils (Figure 4). The β_1 values for the Escambia and Irvington pedons were substantially different; however, no significant differences were observed between the β_1 values of pedons from the same series. In addition, β_1 values involving isolated zones of Fe-accumulation and Fe-depletion were indistinguishable and corresponded with the β_1 values derived from the corresponding whole soil, suggesting that Fe migration to form areas of Fe-accumulation and Fe-depletion incorporated or depleted V in one-to-one correspondence with Fe. Thus, redoximorphic soil features did not show an evidence of V partitioning with respect to Fe.

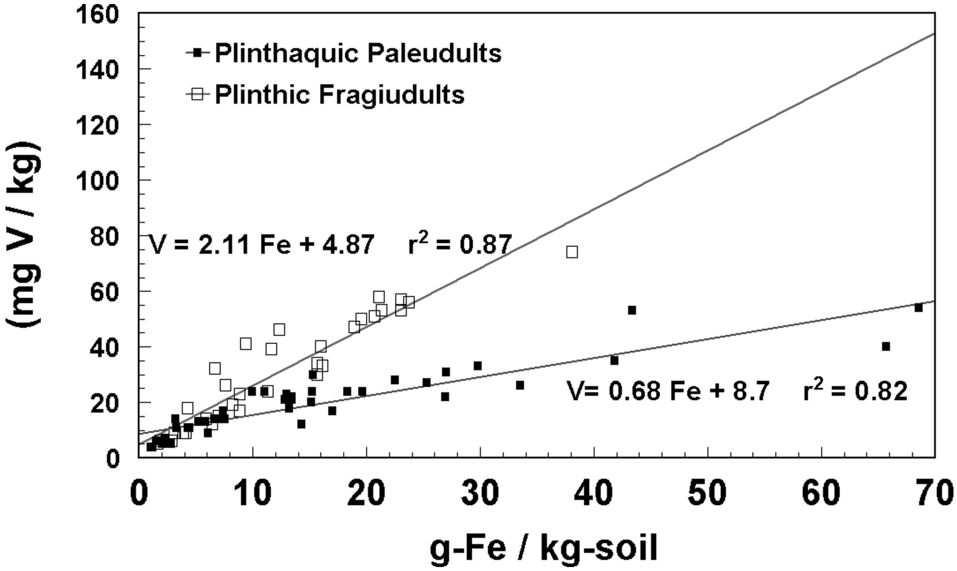

Figure 4. Iron and V relationships for plinthite-bearing coastal-plain soils.

Aqua-regia digestion of the clay fractions show that Fe and V are highly correlated in the Irvington pedons, whereas the Escambia pedons exhibit β_1 values indistinguishable from zero (Figure 5). The clay fractions from the Irvington pedons incorporated Fe and V proportional to their whole soil counterparts; however, their absolute concentrations were somewhat greater than those from whole soil. Conversely, the clay fractions from the Escambia pedons incorporated V to a smaller relative extent than Fe, when based on a whole soil basis.

The Escambia and Irvington pedons generally possess fine sandy loam textures and the small clay contents of the Escambia pedons, coupled with a smaller V/Fe ratio, were not

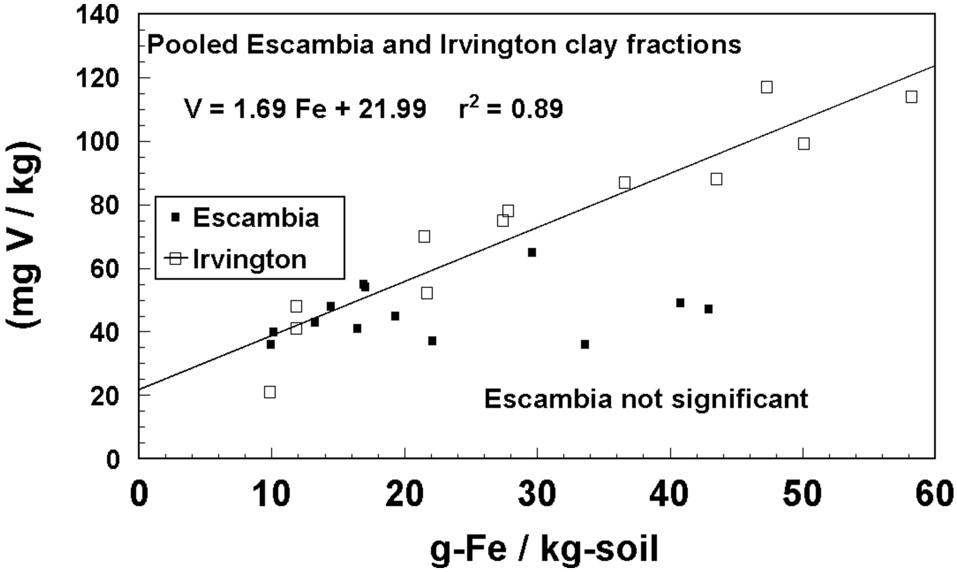

Figure 5. Iron and V relationships for the clay fractions of plinthite-bearing coastal-plane soils.

able to obfuscate the whole soil linear regression relationships. However, the possibility that preferential accumulation of Fe in the clay fraction, coupled with lessivage, could promote illuvial soil horizons having Fe-accumulations is a concern. Eluvial soil horizons exhibiting a larger relative V concentration, as a result of the preferential illuviation of Fe with the clay fraction, could be incorrectly interpreted as V contamination.

Soils Developed in a Combination of Loess and Limestone Residuum

The Scholten (Typic Fragiudalfs), Goss (Paleudalfs) and Hildebrecht (Typic Fragiudalfs) pedons developed in landscapes having a loess mantle resting on highly weathered and acidic limestone residuum. The soil profiles exhibit some mixing of the loess with the underlying residuum (Aide and Marshaus, 2002). The Jonca (Oxyaquic Fragiudalfs) and Menfro (Typic Hapludalfs) pedons were developed entirely loess, with little evidence of mixing with the underlying residuum (Aide and Marshaus, 2002).

All five soil series show linear and positive correspondences between V and Fe. The β_1 values were not significantly different between pooled pedons from the same series (Table 3, Figure 6) and did not reveal any discrete changes in the relationship between Fe and V because of albic, argillic or fragipan soil horizon formation, suggesting that soil forming processes responsible for formation of these diagnostic soil horizons did not selectively partition V with respect to Fe. In the Scholten, Goss and Hildebrecht pedons, mixing of the loess mantle with the underlying residuum did not influence the V and Fe correspondence, a feature attributed to the relatively uniform nature of the parent material mixing throughout the entire soil profile.

The Goss and Scholten pedons were separated into traditional particle size classes. The β_1 values associated with the particle size classes are indistinguishable from those of the whole soil. The absolute Fe and V concentrations are slightly to substantially greater for the sand and clay fractions; however, the Fe and V correspondence was maintained (Figures 7 and 8), suggesting that these fractions did not demonstrate any preference between V and Fe.

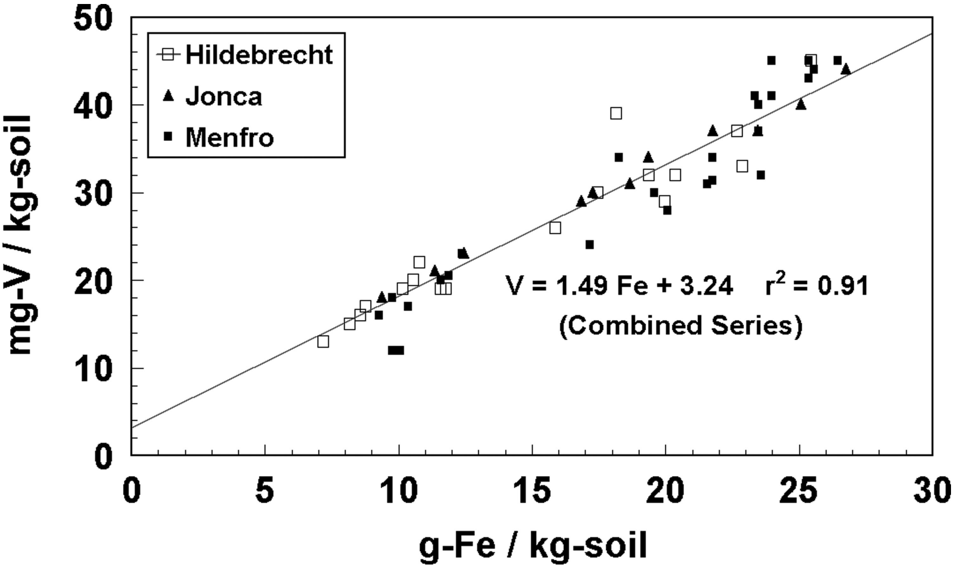

Figure 6. Iron and V relationships for Missouri soils developed primarily in loess.

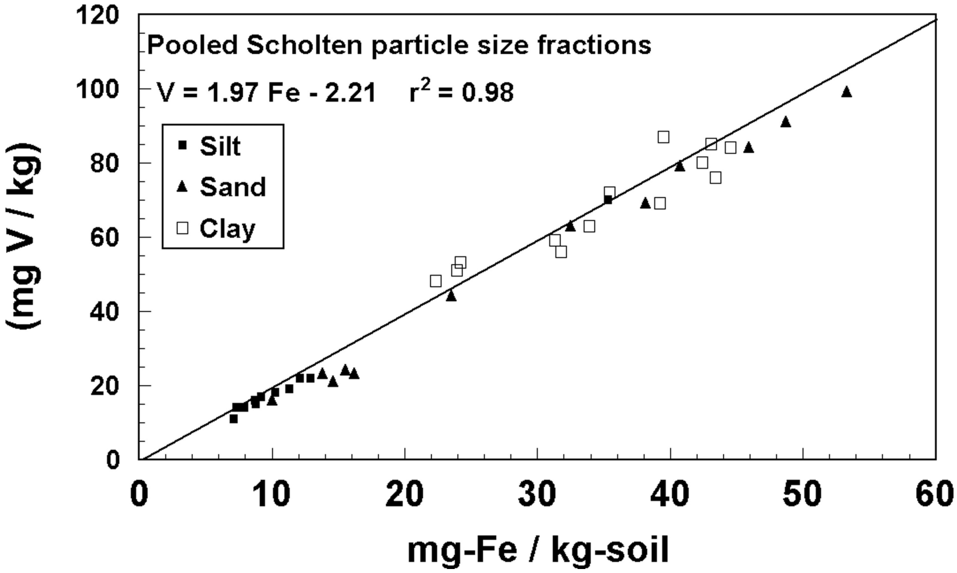

Figure 7. Iron and V relationships for the particle size fractions of the Scholten series.

Discussion

This study intentionally focused on soils having oxic soil environments, with the majority of the pedons exhibiting drainage equal to or better than moderately well-drained. Somewhat poorly-drained soils may present anoxic soil conditions promoting VO_2^+ reduction, while maintaining geothite or hematite stability; however, this Eh window for differential reduction is very narrow. Poorly drained soils likely promote both Fe^{3+} and VO_2^+ reduction, possibly coupled with their leaching removal from the soil system. Thus, we restrict our

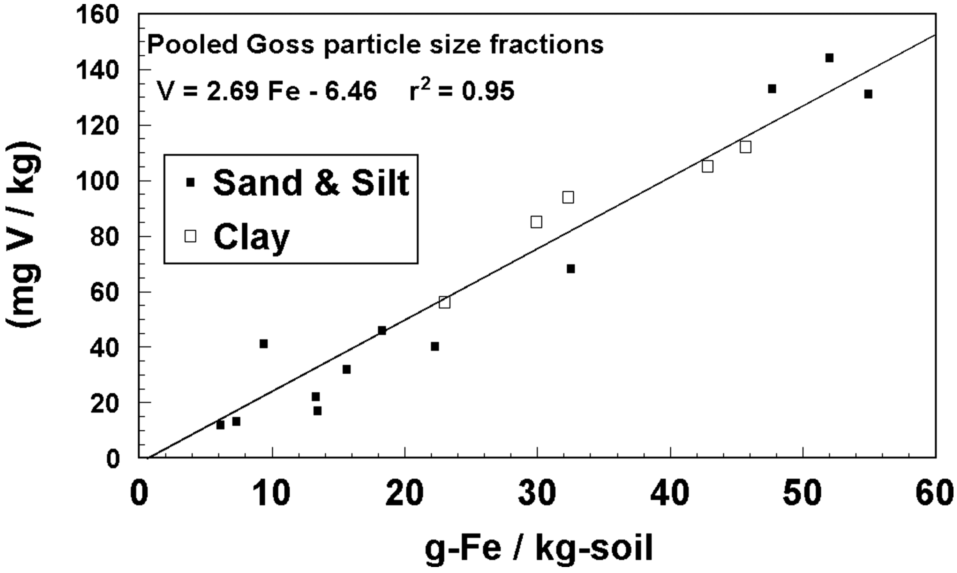

Figure 8. Iron and V relationships for the particle size fractions of the Goss series.

discussion to soils with more oxic soil environments and propose further investigations concerning Fe-V relationships in soils having anoxic soil environments.

This study also confined its attention to soils having ochric and umbric epipedons and subsurface cambic, argillic, calcic and fragic diagnostic soil horizons. No attempt will be made to infer any conclusions for soils having spodic, kandic or gleyed subsurface soil horizons. No sites possessed ultramafic or mafic parent materials.

In general, soils having oxic soil environments reveal V concentrations having linear and positive correspondences with Fe. Exceptions arise when geologic materials involved in the soil forming process have a small Fe and V concentration ranges. Such a case exists with the Lajitas series, which consist of shallow and relatively unweathered soils developed from igneous rock in a semi-arid climate. The Fe and V concentrations from the soils of the Lajitas series are similar to those of the parent materials and the range of the Fe and V concentrations is quite limited. The precise constriction of the Fe and V concentrations in these soils permit the use of the t-test statistic to detect mean separation and to infer any human impact.

The development of argillic and calcic soil horizons do not generally exhibit a relative preference for either Fe or V adsorption. Investigation of several soils in this study indicated statistically equivalent Fe-V relationships between the whole soil and their corresponding clay fractions. However, caution must be maintained because the clay fraction of the Escambia series, located in a coastal-plain setting, did present an appreciably different Fe-V relationship than its whole soil counterpart. If substantial clay fraction-Fe or clay fraction-V preferences are shown to exist, then argillic horizon formation should reduce the whole soil Fe-V relationship.

Plinthite nodules, isolated from the coastal plain soils, did not preferentially accumulate Fe or V relative to their corresponding whole soil counterparts. Considering only the soils in this investigation, oxidation-reduction reactions did not preferentially influence the mobility of Fe with respect to V; however, somewhat poorly drained and poorly drained soils were omitted.

The soils of this investigation ranged from extremely acid to moderately alkaline. Soil organic matter contents similarly varied, as indicated by the presence of umbric and ochric epipedons. Differences in soil acidity and soil organic matter content did not influence the Fe and V correspondence. Eliminating the coarse-textured coastal plain series, the remaining β_1 values ranged from 1.04 to 2.69 (mean of 1.57 and standard deviation of 0.45), suggesting that these predominately fine-silty soils have roughly similar V and Fe correspondences. Attempts to determine statistical trends between β_1 and soil organic matter content, pH, reserve acidity, and soil classification (order level) were unsuccessful.

The Goss and Scholten pedons possess a limestone residuum component and these series show the greatest β_1 value, whereas the soils developed on rhyolite and rhyodacite materials present smaller β_1 values. Soils having intermediate β_1 values commonly have loess or shale as their parent materials. Thus, initial compositions of the parent materials appear to have an appreciable influence on the magnitude of the β_1 values.

An Example of Using V and Fe Correspondence to Infer V Contamination

Reynolds County, Missouri, is a stream dissected Ozark upland landscape with a long history of lead mining. A series of sites along the Bee Creek were selected upstream and downstream from two large tailings ponds. Surface soil samples ($10 \times 10\ \text{cm}^2 \times 6$ cm depth) were obtained and analyzed for Pb, Fe and V using AR digestion (SGS Laboratories, Toronto,

Table 4
Elemental analysis of Control and Lead Mine Tailings Impacted Sites along a watershed in Reynolds County, Missoui

		Mean elemental concentrations			
Treatment	Number of observations	Vanadium $mg \times kg^{-1}$	Lead $mg \times kg^{-1}$	Iron $g \times kg^{-1}$	V/Fe $mg \times g^{-1}$
Control	8	19.1	73.4	10.5	1.91
Impacted	11	16.6	290.9	16.4	1.10
		0.28		0.012	0.001

t-test (probability of mean separation).

Canada). Vanadium concentrations were not significantly different between upstream (control) and downstream (tailings impacted) sites; however, Fe values were greater for the impacted sites (Table 4). The V/Fe ratio was significantly greater for the control sites, inferring that V was not enriched in the impacted sites and all V concentrations are appropriate background concentrations. Lead was substantially enriched in the impacted sites.

A Simple Method for Separating Background and Anthropogenic Vanadium

If it can be established for an array of pristine samples that V and Fe have a consistent relationship, then the presence of anthpogenic V, in otherwise similar samples, should be apparent by a deviation in the V and Fe correspondence. Any Fe additions contributed by the applied slurry should be apparent by inspection of the confidence intervals associated with the mean Fe concentrations of the impacted samples and pristine samples.

Aqua-regia digestion is an excellent protocol for establishing the Fe and V concentrations. The AR extraction is: (1) commercially available at low cost; (2) the accuracy and precision of ICP spectroscopy is excellent for the Fe and V concentrations ranges normally found in the soil environment; (3) HCL and HNO_3 avoid the contamination problems associated with sodium dithionite; and (4) the extraction recovers metals associated with a wide range of labile fractions (soluble, exchangeable, organic, sesquioxides). Alternatively, the 0.2 *M* ammonium oxalate-oxalic acid with 0.3 *M* ascorbic acid as a reductant should be an excellent alternative, particularly if the focus is only on the crystalline sesquioxide fraction (Shuman, 1985).

The method must still be assessed for a greater array of soils, particularly poorly drained soils. The presence of redoximorphic features in the soil profile may indicate anoxic soil conditions that may preferentially segregate Fe and V. Soils having spodic, andic and other diagnostic horizons may similarly have soil processes that effectively partition V and Fe. Soils having a more diverse set of parent materials are potential limitations, particularly if these materials are vertically separated by a lithologic discontinuity.

Another possible limitation is the likelihood that the contaminant has a Fe-V relationship that may mimic the Fe-V relationship of the soil/sediment. In such cases, a selective-sequential extraction should reveal discrete differences of V among the various chemically defined soil fractions. Alternatively, V concentration differences among the particle size fractions may be readily apparent.

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