American Mineralogist, Volume 103, pages 1080–1086, 2018

Analysis and visualization of vanadium mineral diversity and distribution

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ABSTRACT

We employ large mineralogical data resources to investigate the diversity and spatial distribution of vanadium minerals. Data for 219 approved species (http://http://rruff.info/ima, as of April 15, 2016), representing 5437 mineral species-locality pairs (http://http://mindat.org and other sources, as of April 15, 2016), facilitate statistical evaluation and network analysis of these vanadium minerals. V minerals form a sparse, moderately centralized and transitive network, and they cluster into at least seven groups, each of which indicates distinct paragenetic process. In addition, we construct the V mineral-locality bipartite network to reveal mineral diversity at each locality. It shows that only a few V minerals occur at more than three localities, while most minerals occur at one or two localities, conforming to a Large Number of Rare Events (LNRE) distribution. We apply the LNRE model to predict that at least 307 ± 30 (1σ) vanadium minerals exist in Earth's crust today, indicating that at least 88 species have yet to be discovered—a minimum estimate because it assumes that new minerals will be found only using the same methods as in the past. Numerous additional vanadium minerals likely await discovery using micro-analytical methods. By applying LNRE models to subsets of V minerals, we speculate that most new vanadium minerals are to be discovered in sedimentary or hydrothermal non-U-V ore deposits other than igneous or metamorphic rocks/ore deposits.

Keywords: Vanadium, network analysis, statistical mineralogy, LNRE frequency distribution

INTRODUCTION

The last century has seen the discovery of thousands of mineral species. Characteristics of these mineral species, including their physical properties, chemical compositions, and their localities of occurrence, have been parsed into large mineral databases (e.g., http://rruff.info/ima and http://mindat.org). These mineralogical "big data" reveal diversity and spatial distribution of all terrestrial minerals (Hazen et al. 2015a, 2015b, 2016a, 2016b; Hystad et al. 2015a, 2015b, 2016), facilitate network analysis of existing minerals (Morrison et al. 2017), and lead to predictions of Earth's "missing" minerals (Hazen et al. 2016a; Grew et al. 2016; Liu et al. 2017).

This study focuses on the diversity and spatial distribution of all terrestrial vanadium (V) mineral species. V is a redox-sensitive first-row transition element of special interest in geochemistry because it is an ideal oxygen fugacity tracer (Lee et al. 2003; Righter et al. 2016) and might have played a major role in biological electron transfer early in Earth's history (Rehder 2008). In addition, it has strategic importance (National Research Council 2008; Orcutt 2011), environmental impact (Gummow 2011), and human-health significance (Mukherjee et al. 2004). V is a minor element in the crust, averaging ~138 ppm in crustal abundance (Rudnick and Gao 2005), with upper crustal abundance of ~97 ppm (Rudnick and Gao 2005) and lower crustal abundance of ~196 ppm (Rudnick and Fountain 1995). V concentrations vary significantly among different rock types. In igneous rocks, they range from ~40 ppm in ultramafic rocks, and ~60 ppm in granitic rocks, to ~250 ppm in basaltic rocks (Mielke 1979). In sedimentary rocks, the average V content of quartzitic sandstone and pure carbonate sediments is <15 ppm, with higher values in greywackes (40 to 150 ppm) and shales (90 to 260 ppm) (Koljonen 1992). Most V is incorporated into rock-forming minerals as a trace element (e.g., Curtis 1964; Huang et al. 2015), since V^{3+}, V^{4+}, and V^{5+} readily substitute Fe^{3+}/Al^{3+}, Ti^{4+}, and P^{5+} in many common minerals. That being said, crystal-chemical behavior of V cations is not exactly the same as the substituted cations (e.g., Schindler and Hawthorne 1999; Schindler et al. 2000). For instance, V^{4+} and V^{5+} can develop one to two strong π-bonds with oxygen forming either [3+2] or [4+1] coordination geometries, which allows VOx polyhedra to polymerize to sheets and chains but does not allow their incorporation into a three-dimensional network. Similarly, V^{3+} has electronic degeneracy that can drive spontaneous distortions of its coordination polyhedra. Therefore,

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0003-004X/18/0007–1080$05.00/DOI: http://doi.org/10.2138/am-2018-6274

despite its extensive substitution into common minerals as a trace element, the unique crystal chemistry of V enables the formation of 219 minerals with V as an essential element (http://rruff.info/ima as of April 15, 2016; Downs 2006). This limited number of species makes it possible to complete a comprehensive survey of vanadium mineral species and their localities.

A SURVEY OF V MINERAL COMPOSITIONS

Of the 72 essential chemical elements found in all mineral species (http://rruff.info/ima; Hazen et al. 2015a), 44 are essential constituents of vanadium minerals (Table 1). The most frequently encountered elements are oxygen (in 211 species) and hydrogen (147). Next in abundance are common rock-forming elements Ca (51), Si (37), Al (31), Fe (30), Na (29), Cu (28), Mn (26), Ba (20), and Pb (20). The remaining 33 elements are each represented by fewer than 20 species. The number of essential elements in each V mineral range from 1 (the mineral vanadium: V) to 9 [the mineral hanjiangite: $Ba_2Ca(VAl)(AlSi_3O_{10})(OH)_2F(CO_3)_2$], with most species containing more than three essential elements. Average chemical complexity, here defined as numbers of major elements per formula, of all 219 V minerals is 4.6 elements per species, and the values are similar among V^{3+} (5.1 elements per species), V^{4+} (4.4), and V^{5+} species (4.7). However, different groups of elements are incorporated into V^{3+}, V^{4+}, and V^{5+} minerals. Lithophile elements, including Si, Al, Ti, Ba, and B, are more likely present in V^{3+} species, since V^{3+} has an ionic radius (78 pm), similar to Cr^{3+} (75.5 pm) and Fe^{3+} (69 pm; 78.5 pm, high spin), and is incorporated into octahedral sites in many rock-forming minerals. Hydrogen, alkalis, alkaline earth elements, chlorine, UO^{2+} and divalent transition elements (Mn, Cu, Pb, Zn) are found mostly in V^{5+} minerals, where they bind with vanadate ion (VO_4^{3-}) to form sedimentary and hydrothermal minerals. Sulfur and phosphorus are found mostly in V^{4+} species, in which vanadium is present as VO^{2+}, and precipitate as sulfates and phosphates in sedimentary rocks.

Paragenesis of V minerals is closely related to V oxidation states. In general, V^{3+} minerals are of igneous, metamorphic, or hydrothermal origins, with V^{3+} occupying octahedral sites of minerals, the majority of which are silicates. V^{5+} minerals are generally of oxidative hydrothermal and weathering origin, and the majority of them are vanadates. In V^{4+} minerals, V is mostly present as VO^{2+}, which can co-occur with V^{3+}, vanadate ion (VO_4^{3-}), and many other cations (e.g., Ca^{2+}, Sr^{2+}, Cu^{2+}) and anions (e.g., SO_4^{2-}, PO_4^{3-}). Thus they are of mixed origins, including metamorphic, hydrothermal, and oxidative weathering phases, such as various minerals including silicates, sulfates, phosphates, and vanadates.

TABLE 1. Coexisting essential elements in 219 V minerals; numbers for these coexisting elements are based on mineral species and chemical formulas in rruff.info/ima as of April 15, 2016

Element	V Total	V^{3+}	V^{4+}	V^{5+}	Element	V Total	V^{3+}	V^{4+}	V^{5+}
O	211	38	51	144	B	4	4		
H	147	22	39	105	Cr	3	2		1
Ca	51	9	18	35	F	3	1	1	1
Si	37	21	8	9	Ni	3			3
Al	31	11	5	18	Ce	2	1		1
Fe	30	7	6	23	La	2	1		1
Na	29	4	7	24	Li	2		1	1
Cu	28		1	26	N	2			2
Mn	26	4	1	21	Sb	2		1	1
Ba	20	8	5	8	Sn	2			2
Pb	20			20	Tl	2		2	
Mg	17	5	2	11	Ag	1			1
S	17		10	6	Be	1	1		
K	15	1	5	13	C	1	1		
U	14			14	Co	1			1
Ti	12	10	1	2	Cs	1			1
P	10	1	5	4	Ge	1			1
As	7	1	4	6	Hg	1			1
Bi	7			7	Nd	1			1
Cl	7	1		6	Te	1			1
Zn	6			6	W	1		1	1
Sr	5		2	3	Y	1			1

NETWORK ANALYSIS OF TERRESTRIAL V MINERALS

Network analysis has been recently applied to study the diversity and distribution of terrestrial minerals (Morrison et al. 2017). Quantification of network metrics, together with clustering analysis, cannot only visualize mineral coexistence, but also reveal hidden topologies and phase relations in a mineral network.

We perform network analysis on all 219 IMA-approved vanadium minerals, following the methods applied in Morrison et al. (2017), briefly described as follows. The V mineral network is constructed based on mineral co-occurrences. In the network (Fig. 1a), each circular node indicates a V mineral, and each link connecting two nodes indicates a coexisting mineral pair. The color of each mineral node indicates the paragenetic mode, the size of each mineral node is proportional to the number of localities, at which that mineral is known, and the length of each link is inversely proportional to the co-occurrence frequency of the mineral pair. Based on these parameters, a force-directed graph of the V mineral network is generated by algorithms running through several iterations, displacing the nodes according to the attractive and repulsive forces that they exert on each other, until a layout is found that minimizes the "energy" of the system. Force-directed graphs are browser-based, created using the D3 4.0 d3-force module that simulates physical forces using velocity Verlet integration (Verlet 1967) and implements the Barnes-Hut approximation (Barnes and Hut 1986) for performing *n*-body simulations, analogous to those of planetary systems.

To quantify and characterize V mineral networks, we tabulate the V mineral network metrics together with those of Cr and Cu minerals (Table 2). Definition of the network metrics is based on Newman (2013). Given a network with $|N|$ nodes and $|E|$ edges, definitions of the network metrics are described as follows. Edge density is defined as the ratio of $|E|$ divided by potential edge number $[|N|\cdot(|N|-1)/2]$. Let C_i represent the number of edges connecting node i, and C* represent $\max\{C_1, C_2,...,C_{|N|}\}$, then degree centralization is defined as $\Sigma(C^* - C_i)/(|N|^2 - 3|N| + 2)$. Transitivity is defined as 3 times the ratios between the number of triangles and the number of the connected triples of nodes in the network. Diameter is defined as is the shortest

TABLE 2. Network metrics for total V, total Cu, and total terrestrial Cr minerals

Networks	Edge density	Degree centralization	Transitivity	Diameter	Mean distance
V all	0.09350258	0.4064974	0.5030392	5	2.31707
Cu all	0.1210042	0.6841906	0.4784716	4	1.932573
Cr terrestrial	0.0528945	0.3251543	0.4400466	6	2.650876

Note: Metric values for Cu and Cr mineral networks are based on Morrison et al. (2017) (see text for discussion).

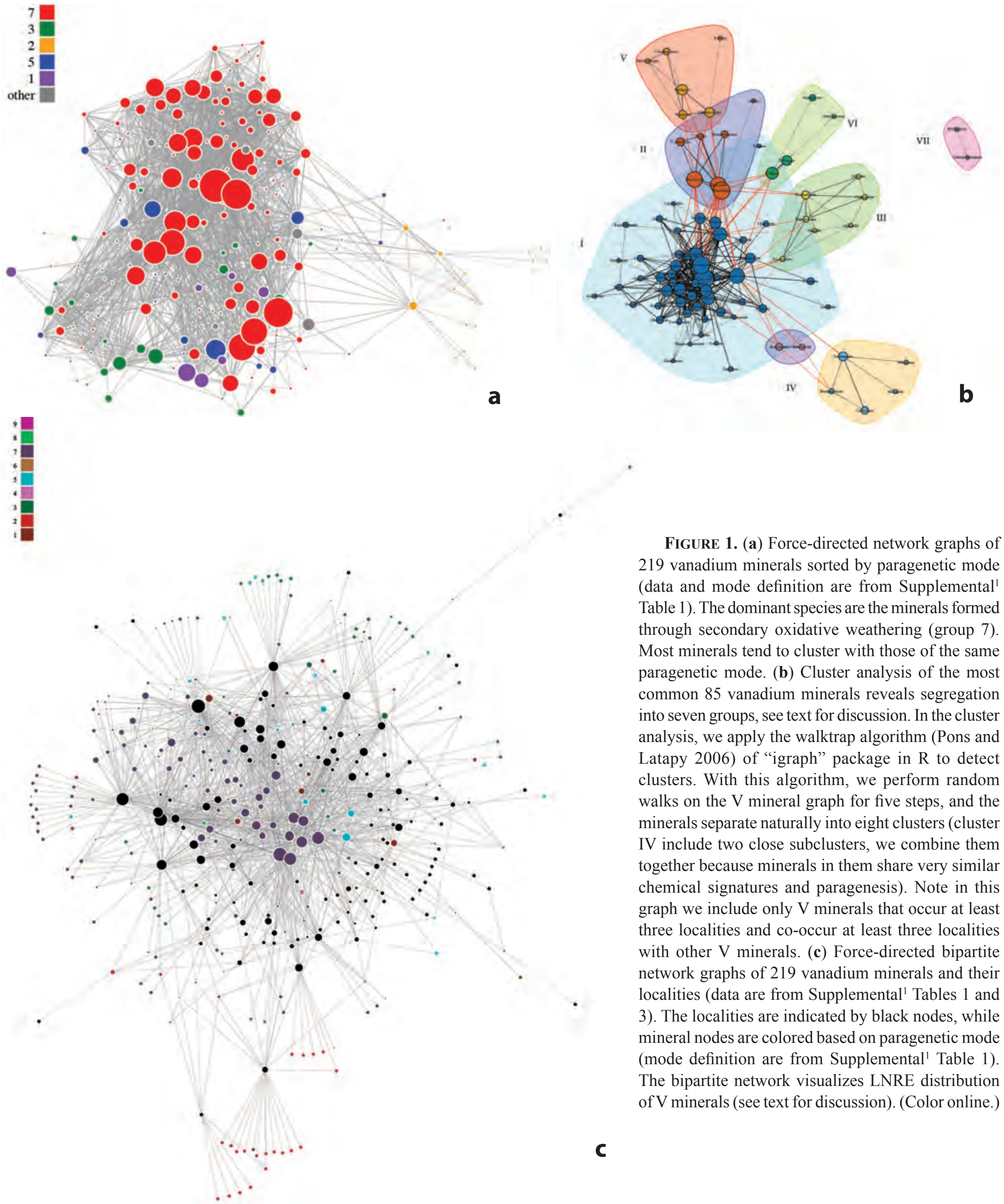

FIGURE 1. (**a**) Force-directed network graphs of 219 vanadium minerals sorted by paragenetic mode (data and mode definition are from Supplemental[1] Table 1). The dominant species are the minerals formed through secondary oxidative weathering (group 7). Most minerals tend to cluster with those of the same paragenetic mode. (**b**) Cluster analysis of the most common 85 vanadium minerals reveals segregation into seven groups, see text for discussion. In the cluster analysis, we apply the walktrap algorithm (Pons and Latapy 2006) of "igraph" package in R to detect clusters. With this algorithm, we perform random walks on the V mineral graph for five steps, and the minerals separate naturally into eight clusters (cluster IV include two close subclusters, we combine them together because minerals in them share very similar chemical signatures and paragenesis). Note in this graph we include only V minerals that occur at least three localities and co-occur at least three localities with other V minerals. (**c**) Force-directed bipartite network graphs of 219 vanadium minerals and their localities (data are from Supplemental[1] Tables 1 and 3). The localities are indicated by black nodes, while mineral nodes are colored based on paragenetic mode (mode definition are from Supplemental[1] Table 1). The bipartite network visualizes LNRE distribution of V minerals (see text for discussion). (Color online.)

distance between the two most distant nodes in the network. In other words, once the shortest path length from every node to all other nodes is calculated, the diameter is the longest of all the calculated path lengths. Mean distance is defined as the mean of all the calculated path lengths. Calculation of these metrics are based on (Csardi and Nepusz 2006), and their implications are described as follows. The V mineral network has a low edge density (0.093), meaning that most V mineral species only coexist with a small fraction of V minerals, possibly those of the same paragenetic origin, similar to the other two networks (Morrison et al. 2017). Transitivity is ~0.5, indicating that half of all coexisting mineral pairs also co-occur with a third mineral. The V mineral network is slightly more centralized (degree centralization of ~0.41), and more packed (diameter of 5, and mean distance of ~2.3) than the Cr mineral network, but much less centralized, and less packed than the Cu mineral network. These metrics are consistent with diversified V mineralization in a wide range of paragenetic environments.

Cluster analysis employs mineral network data to identify subsets of closely related species—an approach that can reveal previously unrecognized relationships among species. We performed cluster analysis to the 85 commonest V minerals (Fig. 1b). Without any supervision, these V mineral nodes separate naturally into seven clusters, faithfully tracking their host ore/rock types. We employed the walktrap algorithm of Pons and Latapy (2006) to detect clusters. This method uses five-step random network walks, which are more likely to stay within a single cluster because fewer of their edges lead to different clusters.

Clustering analysis of V minerals reveals seven different subgroups. The most common V minerals (e.g., carnotite, vanadinite, and tyuyamunite) belong to clusters I and II, which are located in the center and connect to most other clusters (Fig. 1b). Cluster I is the largest, composed of 52 minerals associated with U-V deposits, formed through oxidative weathering or low-*T* hydrothermal alterations, while cluster II is composed of 7 V minerals discovered in oxidative zones of Pb-Zn ores. Minerals in each of the other five clusters are found in specific environments or associated with specific ore deposits, and no connection exists among them. Cluster III minerals are mostly Mn vanadates formed in metamorphic Fe-Mn ores (Brugger et al. 2003), and they could co-occur with vanadates from clusters I and II in Mn-deficient zones. Cluster IV is composed of V^{3+} minerals formed during high-grade (>500 °C) metamorphism, and its connection to cluster I indicates retrograde alteration or prograde metamorphism (Ito 1965). Cluster V minerals are associated with bismuth ores formed in pegmatites (Foord 1996), or via epithermal ores enriched in heavy metals (e.g., Bi, Pb, Te, and occasionally Au; Collier and Plimer 2002), and thus it is connected to cluster II (Pb-Zn ores). Cluster VI minerals are associated with hydrothermal Cu ores that are rich in sulfides and sulfosalts (e.g., Nelson 1939), and minerals in this cluster can be oxidized into those in clusters I and II during ore oxidation (Kampunzu et al. 2009). Cluster VII is isolated from all others, since both minerals (VO^{2+} sulfates) in it are discovered in fossilized woods (Hawthorne et al. 2001; Schindler et al. 2003), distinct from paragenetic environments for minerals in other clusters.

In addition to V mineral network and clustering analysis, we constructed a V mineral-locality bipartite network (Fig. 1c) to reveal mineral diversity at each locality. In this network, each circular node indicates a V mineral (non-black) or a locality (black), and each link connecting two nodes indicates occurrence of one mineral at one locality. Similar to the V mineral network, the V bipartite network is also force-directed, generated by algorithms running through several iterations, displacing the nodes according to the attractive and repulsive forces that they exert on each other. There are only a few of the common V minerals located at the center of the diagram, each connecting to many locality nodes. By contrast, most V minerals are situated along the peripheral areas, and are connected to only one or two localities. The bipartite network thus embodies a Large Number of Rare Events (LNRE) frequency distribution (Baayen 2001; Evert and Baroni 2008) for terrestrial V minerals, i.e., a few V mineral species occur at many localities, but most V minerals are present only at a few localities. Furthermore, the bipartite network also reveals many rare minerals that are formed in paragenetic environments unidentified by clustering analysis. For instance, a couple locality nodes of volcanic fumaroles, Izalco Volcano in El Salvador and Tolbachik Volcano in Kamchatka of Russia, are observed outlying from most others (Fig. 1c), and each is connected to a group of isolated mineral nodes. This topology indicates that V minerals seldom occur in volcanic fumaroles but, when they do, they are present as various rare species.

STATISTICAL ANALYSIS OF TERRESTRIAL V MINERALS

Hystad et al. (2015) discovered that the distribution of all terrestrial minerals conforms to a LNRE frequency distribution. This distribution pattern was later reported for the minerals of carbon, boron, cobalt, chromium, and other elements (Hazen et al. 2016a, 2016b; Grew et al. 2016; Liu et al. 2017). We modeled the frequency distribution of vanadium minerals based on the numbers of known localities for each of the 219 approved vanadium minerals. The easiest approach to estimate the number of localities for each species is to interrogate the crowd-sourced data resource http://mindat.org, which tabulates locality information for every mineral species. To minimize errors arising from uncritical use of http://mindat.org locality data, we examined and updated the raw V-mineral species-locality data by removing geographically redundant localities on http://mindat.org, while adding missing localities cited in the *Handbook of Mineralogy* (Anthony et al. 2003) but not in http://mindat.org (Hazen et al. 2016b; Liu et al. 2017).

There are 5437 V-mineral species-locality data pairs in total, with 66 species recorded at only one locality, an additional 33 species at exactly 2 localities, and 22 species at exactly 3 localities (Supplemental[1] Table 1). By contrast, the 11 most common vanadium minerals account for more than 70% of all species-locality data. This pattern of species distribution among localities, with a few common species and many more rare ones, is typical for the whole set, as well as for various subsets of minerals (Hazen et al. 2015a, 2016a; Hystad et al. 2015b; Grew et al. 2016).

The V-mineral species-locality data are fit to a finite Zipf-Mandelbrot (fZM) model (Hystad et al. 2015a). The fZM parameters for bulk V-mineral species ($\alpha = 0.4855164$; $A = 0.000063038$; $B = 0.1490914$; P-value = 0.17) facilitate modeling of a V-mineral accumulation curve (Fig. 2), with a prediction of at least 307 vanadium minerals in total. In other words, at least 88 V minerals on Earth have not been described. Errors of the fZM model are estimated in a brute-force Monte-Carlo method for bulk V-mineral species, described as follows. Occurrence probabilities were first calculated for each species in the population of 293 V minerals (including both existing and missing species). Based on these probabilities, 500 random samples of size $N = 5437$ (species-locality pairs) were taken from this population. For each sample, a fZM LNRE model was refitted and the expected population size S for each sample was calculated. The standard deviation of the population size (S) of all 500 random samples was calculated as an error estimation of the fZM model. The

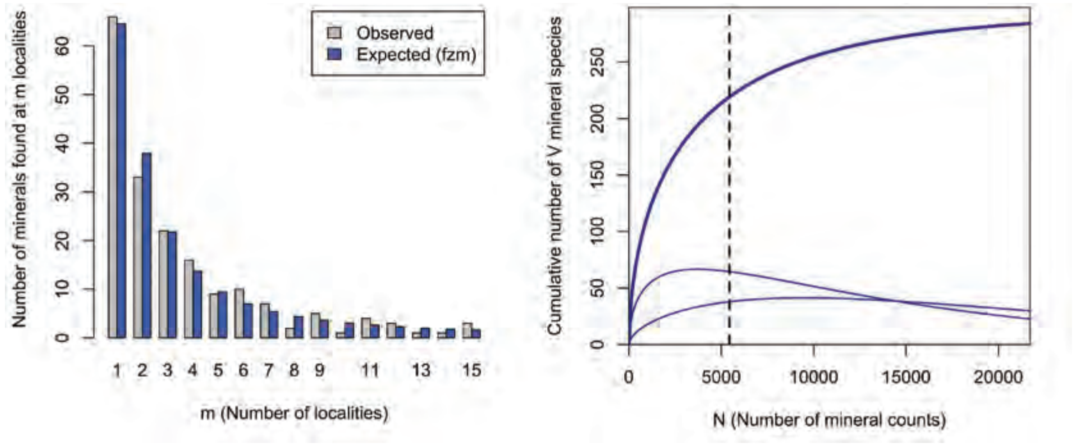

FIGURE 2. (**a**) Frequency spectrum analysis of 219 V-bearing minerals, with 5437 individual mineral-locality data (from http://mindat.org as of April 15, 2016), a finite Zipf-Mandelbrot (fZM) method to model the number of mineral species for minerals found at exactly 1 to 15 localities (Hystad et al. 2015a). (**b**) This model facilitates the prediction of the mineral species accumulation curve (upper curve, "all"), which plots the number of expected V mineral species (*y*-axis) as additional mineral species/locality data (*x*-axis) are discovered. The vertical dashed line indicates data recorded as of April 15, 2016 in mindat.org, as well as locality data from the *Handbook of Mineralogy* (Anthony et al. 2003) and systematic searching under each mineral name in Georef. The model also predicts the varying numbers of mineral species known from exactly one locality (curve 1) or from exactly two localities (curve 2). Note that the number of mineral species from only one locality is now decreasing, whereas the number from two localities is now increasing. We predict that the number of minerals known from two localities will surpass those from one locality when the number of species-locality data exceeds ~13 000. (Color online.)

resulting analysis suggests a standard deviation of 30 species for bulk V minerals.

IMPLICATIONS

The 219 known V-mineral species represent only a small fraction of the thousands of known inorganic V compounds [International Crystal Structure Database (http://icsd.fiz-karlsruhe.de)]. Vanadium, as all other elements, has the potential to form thousands of mineral species (Hazen et al. 2015b); however, far fewer V mineral species have formed on Earth because of the special geochemical conditions required to concentrate vanadium. Prediction of the exact chemistry, location, and paragenesis of most new V mineral species is unlikely. However, characteristics of the possible missing V minerals, including their chemistry and paragenesis, can be constrained by a Large Number of Events (LNRE) modeling of V mineral subsets.

We first applied LNRE-fZM models and performed error analysis to subsets of vanadium minerals categorized by the V oxidation state (Table 3). For V^{5+} minerals, the model predicts that at least 38 ± 21 (1σ) species await discovery. However, for V^{3+} and V^{4+} minerals, the fZM model predicts unreasonable numbers of undiscovered species, and the Monte-Carlo error analysis cannot render convergent results (Table 3). This problem is likely due to the fact that the sample size is small (554 and 495 species-locality pairs for V^{3+} and V^{4+} minerals, respectively) but relatively large (4678 species-locality pairs) for V^{5+} minerals.

In addition, we applied LNRE-fZM models and performed error analysis to V mineral subsets of rock-forming species (i.e., minerals composed of Si, Al, or Ti) and non-rock-forming V-O salts (i.e., minerals containing V, O, and devoid of Si, Al, and Ti). Note these two subsets are independent from those categorized based on vanadium valences. For rock-forming species, the model predicts that at least 26 ± 12 (1σ) species are missing. In comparison, for non-rock-forming V-O salts, the model suggest at least 52 ± 19 (1σ) are yet to be discovered.

Furthermore, we applied LNRE-fZM models and performed error analysis on various subsets of V mineral defined by cluster analysis. To be specific, we analyzed one subset that includes V minerals discovered in U-V ore deposits, and a second subset that includes all other species. All non-U-V-deposit clusters are combined for LNRE modeling since the sample size is too small in each. For V minerals from U-V deposits, the model predicts only 9 ± 8 (1σ) undiscovered species, suggesting most V minerals in U-V deposits have been documented. This prediction is not

TABLE 3. Estimations of undiscovered species numbers for V minerals in total and in subsets, calculated from a finite Zipf-Mandelbrot (fZM) model

	Total	$V^{3+/4+}$	V^{5+}	Rock-forming	Non-rock-forming	U-V deposits	Non-U-V
Alpha	0.4855164	0.60341	0.4308936	0.8616267	0.4273307	0.1914736	0.8193236
A	6.30E-05	0.000333064	8.43E-05	0.001081167	7.38E-05	0.000181891	0.000201085
B	0.1490914	0.4659284	0.1778848	1.097291	0.1776986	0.120249	4.194793
P-value	0.1683843	0.6790167	0.1856256	0.4376919	0.4577854	0.4439887	0.4517901
Current species	219	70	149	66	153	78	142
Estimated total	307	117	196	92	205	87	218
To be discovered	88	47	47	26	52	9	76
Error	30	24	21	12	19	8	34
Sample size	5437	759	4678	492	4945	3438	1999

Notes: Parameters of the fZM model are listed. See text for discussion.

surprising since V mineral species (e.g., carnotite and tyuyamunite) in U-V deposits are typically colorful and well crystallized, and thus easier to be collected and identified in hand specimen. In contrast, many more V minerals, up to 76 ± 34 (1σ) species, are yet to be discovered for non-U-V deposits. The modeling result is consistent with the bipartite network (Fig. 1c) which shows that many rare V minerals are formed in uncommon paragenetic environments (e.g., volcanic fumaroles).

To summarize, for the missing V minerals, the LNRE modeling on different V-mineral subsets suggests that about a half may be V^{5+} species, and the other half are $V^{3+/4+}$ minerals; a third may be present as rock-forming minerals, and two thirds may exist as non-rock-forming V-O salts; and most species are likely to be discovered in paragenetic environments other than U-V ore deposits.

In addition to LNRE predictions, we also tabulate 660 synthetic V compounds (Supplemental[1] Table 2) that have not been discovered in nature, but are speculated to occur on Earth (or on other highly differentiated planets) as new mineral species. These potential V minerals include 7 oxides, 26 sulfides, 6 silicates, 16 uranates, 59 sulfur/selenium/tellurium-oxy acid salts (e.g., sulfates, sulfites, selenates, tellurates), 102 phosphates, 16 arsenates, 70 halides, and 358 others. Most of the stable V silicates have been discovered in nature (37 minerals), and only a few (6 species) are known exclusively as synthetic species. V valences of synthetic V oxides stable at Earth's surface are between +3 and +5, similar to those of discovered V oxides minerals (e.g., karelianite, paramontroseite, and shcherbinaite). We speculate that V oxides and silicates known only as synthetic compounds are most likely to be discovered in metamorphic rocks, fumaroles, or hydrothermal U-V deposits, similar to previously discovered species. Synthetic stable V-bearing sulfides could contain V^{3+}, V^{4+}, or V^{5+}, many of which share similar crystal structures to V/transition metal minerals (Supplemental[1] Table 2). For instance, two V sulfides share structures similar to colimaite, and a group of synthetic V sulfides exhibit a spinel structure, similar to some metal Cr sulfide minerals (e.g., brezinaite and kalininite; Liu et al. 2017). These synthetic V sulfides, if present in nature, are likely to be of hydrothermal origin, since most of V sulfide minerals are found primarily in hydrothermal deposits (Supplemental[1] Table 1). Synthetic V uranates (U^{6+}) yet to be discovered in nature are all anhydrous (Supplemental[1] Table 2), whereas all discovered V uranate minerals are hydrous species, of hydrothermal or secondary weathering origin. Most of the synthetic experiments are performed in anhydrous environments, whereas water is ubiquitously present at the Earth's surface. Therefore, the chances of finding these anhydrous synthetic species in nature are very small.

Association of V with some common anions (e.g., sulfates, phosphates, arsenates, selenates, tellurates, and halides) is observed not only in many minerals (Supplemental[1] Table 1), but also in various synthetic compounds (Supplemental[1] Table 2). Abundances of both minerals and synthetic crystals in this group imply several new V minerals remain to be discovered in hydrothermal, sedimentary, or secondary weathering deposits. In comparison, V carbonates and nitrates are very rare in both discovered minerals and synthetic compounds, indicating very small chances of finding these species in nature.

The remaining synthetic V compounds are dominantly vanadates (Supplemental[1] Table 2). Note that for both mineral and synthetic compounds, the number of phosphates, although quite high, is significantly less than that of vanadates. This difference is due to the fact that crystal-chemical behaviors of V^{5+} and P^{5+} are similar but not identical (Schindler et al. 2000). A few of the vanadate synthetic crystals share similar structures to known V minerals (e.g., cavoite, blossite, and ansermetite). However, the majority of them possess different crystal structures. Chemical compositions of the synthetic vanadates are very diverse, containing most lithophile and chalcophile elements, as well as some siderophile elements, as essential elements. Based on their chemistry (Supplemental[1] Table 2) and the paragenesis of current vanadate minerals (Supplemental[1] Table 1, Fig. 1b), we propose that these synthetic vanadates may be discovered in oxidized zones of Pb-Zn or other heavy metal (e.g., Bi and Te) ore deposits.

ACKNOWLEDGMENTS

This manuscript is greatly benefited from thorough reviews from Michael Schindler and Sergey Krivovichev. We are also grateful for Fernando Colombo's reviewing and handling the manuscript. This work was supported in part by the Deep Carbon Observatory, the Alfred P. Sloan Foundation, the W.M. Keck Foundation, a private foundation, NASA, and the Carnegie Institution for Science for support of mineral evolution and ecology research.

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Manuscript received August 11, 2017
Manuscript accepted March 23, 2018
Manuscript handled by Fernando Colombo

Endnote:

[1] Deposit item AM-18-76274, Supplemental Tables. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2018/Jul2018_data/Jul2018_data.html).