

## MINERAL ECOLOGY: CHANCE AND NECESSITY IN THE MINERAL DIVERSITY OF TERRESTRIAL PLANETS

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### ABSTRACT

Four factors contribute to the roles played by chance and necessity in determining mineral distribution and diversity at or near the surfaces of terrestrial planets: (1) crystal chemical characteristics; (2) mineral stability ranges; (3) the probability of occurrence for rare minerals; and (4) stellar and planetary stoichiometries in extrasolar systems.

The most abundant elements generally have the largest numbers of mineral species, as modeled by relationships for Earth's upper continental crust (E) and the Moon (M), respectively:

$$\text{Log}(N_E) = 0.22 \text{Log}(C_E) + 1.70 (R^2 = 0.34) (4861 \text{ minerals, } 72 \text{ elements})$$

$$\text{Log}(N_M) = 0.19 \text{Log}(C_M) + 0.23 (R^2 = 0.68) (63 \text{ minerals, } 24 \text{ elements}),$$

where  $C$  is an element's abundance in ppm and  $N$  is the number of mineral species in which that element is essential. Several elements that plot significantly below the trend for Earth's upper continental crust (*e.g.*, Ga, Hf, and Rb) mimic other more abundant elements and thus are less likely to form their own species. Other elements (*e.g.*, Ag, As, Cu, Pb, S, and U) plot significantly above the trend, which we attribute to their unique crystal chemical affinities, multiple coordination and oxidation states, their extreme concentration in some ore-forming fluids, and/or frequent occurrence with a variety of other rare elements—all factors that increase the diversity of mineral species incorporating these elements. The corresponding diagram for the Moon shows a tighter fit, most likely because none of these elements, except Cu and S, are essential constituents in lunar minerals. Given the similar slopes for Earth and the Moon, we suggest that the increase in mineral diversity with element abundance is a deterministic aspect of planetary mineral diversity. Though based on a limited number of collecting sites, the Moon's observed mineralogical diversity could be close to the minimum for a rocky planet or moon comparable in size—a baseline against which diversity of other terrestrial planets and moons having radii in the same range as Earth and its Moon can be measured. Mineral-forming processes on the Moon are limited to igneous activity, meteor impacts, and the solar wind—processes that could affect any planet or moon. By contrast, other terrestrial planets and moons have been subjected to more varied physical, chemical, and (in the case of Earth) biological processes that can increase mineral diversity in both deterministic and stochastic ways.

Total mineral diversity for different elements is not appreciably influenced by the relative stabilities of individual phases, *e.g.*, the broad pressure-temperature-composition stability ranges of cinnabar (HgS) and zircon (ZrSiO<sub>4</sub>) do not significantly diminish the diversity of Hg or Zr minerals. Moreover, the significant expansion of near-surface redox conditions on Earth through the evolution of microbial oxygenic photosynthesis tripled the available composition space of Earth's near-surface environment, and resulted in a corresponding tripling of mineral diversity subsequent to atmospheric oxidation.

Of 4933 approved mineral species, 34% are known from only one or two localities, and more than half are known from five or fewer localities. Statistical analysis of this frequency distribution suggests that thousands of other plausible rare

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mineral species await discovery or could have occurred at some point in Earth's history, only to be subsequently lost by burial, erosion, or subduction—*i.e.*, much of Earth's mineral diversity associated with rare species results from stochastic processes.

Measurements of stellar stoichiometry reveal that stars can differ significantly from the Sun in relative abundances of rock-forming elements, which implies that bulk compositions of some extrasolar Earth-like planets likely differ significantly from those of Earth, particularly if the fractionation processes in evolving stellar nebulas and planetary differentiation are factored in. Comparison of Earth's upper continental crust and the Moon shows that differences in element ratios are reflected in ratios of mineral species containing these elements.

In summary, although deterministic factors control the distribution of the most common rock-forming minerals in Earth's upper continental crust and on the Moon, stochastic processes play a significant role in the diversity of less common minerals. Were Earth's history to be replayed, and thousands of mineral species discovered and characterized anew, it is probable that many of those minerals would differ from species known today.

**Keywords:** Statistical mineralogy, mineral evolution, mineral ecology, crystal chemistry, planetary stoichiometry, philosophy of mineralogy, frequency distributions, LNRE distributions, diversity, disparity, island biogeography.

## INTRODUCTION

Complex systems evolve through a combination of deterministic and stochastic processes (Pellegrini *et al.* 2003, Rice 2008, Lecca *et al.* 2013). By necessity, all evolving systems must conform to chemical and physical laws, but chance events also play an important role, leading to unpredictability and “frozen accidents” in some details of these systems.

Earth's changing near-surface mineralogy through 4.5 billion years of planetary history has displayed characteristics typical of other complex evolving systems, including congruency, diversification, stasis, punctuation, and extinction (Hazen *et al.* 2008, Hazen & Eldredge 2010). Many aspects of planetary mineralogy, including the prevalence of the most abundant rock-forming phases, are deterministic aspects of mineral evolution. Thus, the diversity and distribution of minerals in Earth's near-surface environments in the past, as well as on terrestrial planets in other star systems, should display broad similarities to Earth today. In particular, the fact that O, C, Mg, Si, S, and Fe are the most abundant elements in the solar system (>3% in CI chondrites: Palme & Jones 2005, Lodders 2010) implies that a relatively few familiar rock-forming oxide and silicate minerals will volumetrically dominate the crust and mantle of any rocky planet or moon, not only in our solar system, but also in other systems in our galaxy and beyond. However, chance may also play an important role in mineralogical details (Grew & Hazen 2014). Accordingly, the objectives of this contribution are to consider two related questions: (1) Why do we see the compositional and spatial distributions of the nearly 5000 mineral species observed today on Earth and the Moon, as well as in meteorites (*i.e.*, what aspects of mineral diversity are deterministic)? and (2) How similar or different would that mineralogy be if one “played the tape of Earth's history over again,” or if we could survey the mineralogy on a different terrestrial planet (*i.e.*, what are the roles of varied initial conditions

and contingency)? Thus we address questions of chance and necessity in the “ecology” of minerals—questions that have received scant attention in treatments of mineral evolution prior to Grew & Hazen (2014).

The relative roles of chance and necessity have been a matter of considerable debate in studies of the origins and evolution of life (Monod 1971, Lecca *et al.* 2013, Davila & McKay 2014). For example, carbon is almost universally cited as the inevitable central element in any plausible biochemistry (Hazen 2005, and references therein). At the molecular scale, several theories of life's origins invoke deeply rooted biomolecular pathways, notably the TCA metabolic cycle, as deterministic aspects of life (Morowitz *et al.* 1988, 2000, Wächtershäuser 1988, 1990, 1992, Morowitz 1992). By contrast, some molecular biologists view the details of the genetic code as a “frozen accident” (Crick 1968, Freeland & Hurst 1998); *i.e.*, combinations of three nucleobases (codons) that correspond to specific amino acids may be largely the result of historical contingency. However, subsequent analyses and ongoing lively debates continue to assess possible deterministic aspects of the genetic code (Gusev & Schulze-Makuch 2004, Vestigian *et al.* 2006, Delarue 2007, Carter 2008), as well as protein structure and function (Harms & Thornton 2014).

In the context of subsequent biological evolution, some authorities have argued for contingency's dominant role, for example in the morphology of Cambrian invertebrates (Gould 1989, 2002). Others point to deterministic aspects of animal evolution, including gastropod topology (Schindel 1990, Noshita *et al.* 2012); arthropod anatomy (Conway-Morris 1998, 2003); protein structure (Zhang & Kumar 1997); and the independent, or “convergent,” evolution of such anatomical features as eyes, limbs, wings, fins, defensive spines, and other functional characteristics (Pearce 2011, Chirat *et al.* 2013, Mahler *et al.* 2013).

In a similar vein, Grew & Hazen (2014) considered the role of chance and necessity in the evolving

TABLE 1. ABUNDANCES OF 72 CHEMICAL ELEMENTS IN EARTH'S UPPER CONTINENTAL CRUST AND THE NUMBER OF MINERAL SPECIES IN WHICH THAT ELEMENT IS ESSENTIAL

Element	Abundance (ppm)	# minerals
O*	472000	3984
Si	311312	1430
Al	81505	1006
Fe	39176	1043
Ca	25657	1197
Na	24259	932
K	23244	447
Mg	14955	620
Ti	3836	333
C <sup>§</sup>	3240	395
H <sup>†</sup>	1520	2817
Mn	774	529
P	655	554
Ba	628	226
F	557	378
Cl	370	362
Sr	320	129
Zr	193	120
V	97	214
Cr	92	84
Rb	84	3
N	83	91
Zn	67	243
Ce	63	146
S	62	1011
Ni	47	144
La	31	45
Cu	28	641
Nd	27	27
Li	24	116
Y	21	119
Ga	17.5	5
Co	17.3	64
Pb	17	505
B	17	263
Sc	14.0	13
Nb	12	146
Th	10.5	35
Hf	5.3	1
Cs	4.9	19
As	4.8	576
Sm	4.7	2
Gd	4.0	1
Dy	3.9	1
U	2.7	252
Er	2.3	1
Be	2.1	112
Sn	2.1	89
Yb	1.96	5
W	1.9	40
Br	1.6	12

TABLE 1. (CONTINUED)

Element	Abundance (ppm)	# minerals
Ge	1.4	28
I	1.4	26
Mo	1.1	60
Ta	0.9	57
Tl	0.9	57
Sb	0.4	245
Bi	0.16	218
Cd	0.09	27
Se	0.09	116
In	0.056	12
Ag	0.053	169
Hg	0.05	93
Te <sup>§</sup>	0.005	159
Au	0.0015	30
Pd	0.00052	62
Pt	0.0005	31
Ru	0.00034	8
Re	0.000198	2
Rh <sup>§</sup>	0.00006	14
Os	0.000031	6
Ir	0.000022	17

Note: \*Continental crust as a whole (Wedepohl 1995); <sup>§</sup>Upper continental crust (Wedepohl 1995); <sup>†</sup>Bowen (1979), as quoted in Emsley (1991). Remaining upper crustal abundances taken from Rudnick & Gao (2005). Mineral numbers from the IMA list of approved minerals (ruff.ima/info; as of 1 June 2014) from which 72 minerals of non-crustal origin have been excluded (see Table 2).

diversification of minerals of the rare element beryllium (2.1 ppm average upper crustal abundance; see Table 1). They concluded that occurrences of the most abundant Be minerals, including beryl ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ), phenakite ( $\text{Be}_2\text{SiO}_4$ ), and chrysoberyl ( $\text{BeAl}_2\text{O}_4$ ), are deterministic aspects of any Earth-like planet, because these phases only require a modest Be concentration mechanism in association with Al and Si. By contrast, the occurrence of many other Be minerals is a matter of chance—a conclusion based on the observation that more than 40 of the 112 Be minerals listed by Grew & Hazen (2014) are known from only a single locality. Rare Be minerals often result from unusual combinations of relatively rare elements (Be with Sb, Sc, Sn, Zn, or Zr, for example), coupled with their fortuitous preservation, exposure, and discovery—these rare phases may be viewed as Earth's mineralogical “frozen accidents.” Consequently, Grew & Hazen (2014) predicted that dozens of rare beryllium minerals await discovery in as yet unexposed subsurface deposits, whereas numerous other plausible phases, including compositional variants of known Be minerals, Be sulfates, Be carbonates, Be halides, Be borates, and Be compounds with Nb, Ta, Th, and U,

may have never formed on Earth, or did not survive subsequent geologic events because of historical circumstances. Grew & Hazen (2014) concluded that the details of Be mineral evolution on other Earth-like planets are likely to have differed from Earth, owing to contingent events.

In this contribution we expand on these ideas by focusing on factors that influence planetary-scale mineral diversity, which we define as the number of different coexisting mineral species. Note that the concept of mineral diversity can be applied to the minerals of specific chemical elements, geographical regions, tectonic settings, or lithologies. In this context, a distinction should be made between mineral “diversity” and “disparity”—two related concepts that are also important in the description of evolving ecosystems (Jaanusson 1981, Runnegar 1987, Gould 1989). Disparity in biology and paleontology refers to the range of morphotypes (or genetic variation) exhibited by an ecosystem. Thus, an ecosystem with three species of algae has the same diversity as an ecosystem with one species of algae, one species of fish, and one species of coral, but the latter ecosystem has greater disparity. Exploration of the concept of the nature and origins of disparity in mineral ecology is the subject of a study now in preparation.

Here we explore four factors that influence mineral diversity: (1) crystal chemical characteristics, as reflected in the relationship between mineral diversity and element abundance; (2) mineral stability ranges in multi-dimensional composition space, as calculated from thermochemical data; (3) the probability of occurrence for rare minerals, based on frequency distribution analysis of mineral species and locality data; and (4) stellar stoichiometries and the compositions of other star systems implicit in recent data obtained in the search for extrasolar Earth-like planets. This contribution, an introduction to an anticipated series of studies on “mineral ecology” and “statistical mineralogy,” thus takes advantage of extensive and growing mineralogical databases which facilitate data-driven “abductive” approaches to discovery (Lehnert *et al.* 2007, Hazen *et al.* 2011, Keller & Schoene 2012, Hazen 2014).

#### MINERALOGICAL DATABASES

Our study is based on the statistical analysis of data provided by open access mineralogical databases. We rely on the list of minerals approved by the Commission on New Minerals, Nomenclature and Classification (formerly the Commission of New Minerals and Mineral Names) of the International Mineralogical Association as of 1 June 2014 (ruff.info/ima; Downs 2006) and on the online compilation of minerals and their localities at mindat.org as of 1 February 2014. These databases have been used in two different ways, depending on

the application. In determining the relationships between element abundance and mineral diversity (see Part I), we have principally employed ruff.info/ima, which provides IMA approved mineral names and idealized chemical formulas.

Part III on mineral frequency distribution relationships employs both ruff.info/ima for identification of approved mineral species, and mindat.org, which tabulates worldwide mineral species and locality information, not only for Earth, but also for the Moon, Mars, meteorites, and interstellar space. The latter database must be employed in statistical studies with caution for several reasons, including: (1) numerous mineral/locality data arise from crowd-sourced contributions, and therefore include unpublished and unconfirmed reports; (2) some mineral names employed in mindat.org are inconsistent with approved IMA species names; (3) different veins or waste dumps from the same mine may be listed as separate localities, thus over-representing the occurrence of some species; (4) reported locality data are significantly biased toward geographical areas with both mines and mineral collectors; (5) colorful and/or crystalline species of interest to mineral collectors may be over-represented compared to colorless and/or poorly crystallized species in locality statistics; and (6) localities for the most common rock-forming minerals are significantly under-reported—indeed, the concept of “locality” has little meaning for essential minerals in the most widespread igneous, metamorphic, and sedimentary lithologies. These concerns necessitated extensive checking of the original literature prior to statistical analysis, as described by Grew & Hazen (2014).

In preparing the list of minerals not considered to have formed in Earth’s upper continental crust (see Part 1), mindat.org served as a primary source of information and was supplemented with some consultation of the original literature, whereas in compiling a list of lunar minerals (see Part I), mindat.org served as a guide to the original literature rather than a source of data. In contrast, for determining mineral frequency distribution relationships (see Part III), we made uncritical use of mindat.org as a source of locality numbers, despite the geographic and other potential biases noted above. Our justification for this approach is that the total number of localities is sufficiently large, and the deficiencies too few, to significantly affect statistical treatment of the locality numbers.

#### PART I: ELEMENT ABUNDANCE—MINERAL DIVERSITY RELATIONSHIPS

##### *Earth’s Upper Continental Crust*

Crystal chemistry and major element composition play dominant roles in the observed distribution of

mineral species (Wenk & Bulakh 2004, Christy 2015). Table 1 records average upper crustal abundances [Rudnick & Gao 2005, supplemented by Wedepohl 1995; Bowen 1979 (as quoted in Emsley 1991)] of the 72 chemical elements cited as essential in International Mineralogical Association (IMA)-approved mineral formulas, as well as the numbers of IMA approved mineral species in which those elements are essential (tabulated at [ruff.info/ima](http://ruff.info/ima); data as of 1 June 2014). We have excluded 72 minerals (Table 2) that have not been found in crustal rocks, including: (1) 66 minerals occurring only in meteorites and other extraterrestrial objects, except that minerals formed by terrestrial weathering of extraterrestrial objects have been included; and (2) two additional minerals exclusively of deep mantle origin formed under extreme pressures. Thirteen minerals, mostly of the elements class, *e.g.*, metals, alloys, carbides, silicides, nitrides, phosphides (Strunz & Nickel 2001), have been reported not only in meteorites or in mantle material, but also in burning dumps, slag, or alluvium, according to [mindat.org](http://mindat.org). However, the natural origin of material from these terrestrial occurrences is questionable, *e.g.*, the doubts surrounding jedwabite, niobocarbide, and tantalcarbide (Fron del 1962, Pekov 1998), and thus these occurrences are not considered to be proof of a crustal origin. Our rationale for excluding minerals in extraterrestrial objects is that they formed from material having a very different bulk composition than that of Earth's upper continental crust; *e.g.*, allendeite ( $\text{Sc}_4\text{Zr}_2\text{O}_{12}$ ) in an ultra-refractory inclusion in the Allende meteorite (Ma *et al.* 2014). It also appears inappropriate to consider that a mineral is crustal if it formed in mantle bulk compositions at pressures in excess of the so-called "ultrahigh" pressures experienced by deeply subducted crustal rocks. However, excluding these 72 minerals has a negligible effect on the relationship between diversity and composition (see below), because only 1.5% of all known minerals have been excluded.

Figure 1A illustrates the log of the number of known mineral species in Earth's upper continental crust *versus* the log of crustal abundance (in ppm) for each of the 72 essential mineral-forming elements. Linear regression analysis of these data (though they are not well correlated for reasons discussed below) reveals a general trend with positive slope; the most abundant crustal chemical elements tend to have the greatest numbers of mineral species. Thus, Earth's most abundant element, oxygen, is present in more than 80% of crustal minerals (3984 of 4861 species), while Si with 1430 species, Ca (1197), Fe (1043), and Al (1006) are abundant crustal cations with the greatest numbers of mineral species. This abundance-diversity relationship is given by:

$$\begin{aligned} \text{Log}(N_E) &= 0.2159 \text{Log}(C_E) \\ &+ 1.6962 (R^2 = 0.34) \quad [\text{Equation 1a}] \end{aligned}$$

where  $C_E$  is the element's abundance in ppm in Earth's upper continental crust and  $N_E$  is the number of IMA-approved crustal mineral species in which that element is essential (Table 1). Note that if all species are included in this calculation, the resulting equation is virtually identical; thus the excluded 72 minerals do not alter the results:

$$\begin{aligned} \text{Log}(N_E) &= 0.2165 \text{Log}(C_E) \\ &+ 1.7011 (R^2 = 0.34) \quad [\text{Equation 1b}] \end{aligned}$$

In summary, after rounding, we can give for Earth's upper continental crust:

$$\begin{aligned} \text{Log}(N_E) &= 0.22 \text{Log}(C_E) + 1.70 (R^2 = 0.34) \\ &[\text{Equation 1}] \end{aligned}$$

In deciding which elements are essential for a mineral to form, we have relied on the formulas in the IMA list at [ruff.info/ima](http://ruff.info/ima). Usually these formulas correspond to compositional endmembers such as  $\text{Mg}_2\text{SiO}_4$  and  $\text{Fe}_2\text{SiO}_4$ . However, in a few cases, major substitutions are given, *e.g.*, buseckite [(Fe,Zn,Mn)S] and hexamolybdenum (Mo,Ru,Fe) (Table 2), in which case only the most abundant element is considered, *i.e.*, FeS and Mo, respectively. This approach in treating mineral compositions means that our tabulations of the number of minerals for each element (Tables 1, 2) are minimum estimates of the diversity of species that incorporate that element.

### The Moon

Earth's moon is the only other planetary body for which sufficient information exists for a similar treatment (Table 3). More than 150 minerals (including 16 unnamed species) are listed on [mindat.org](http://mindat.org) as occurring on the Moon. However, it is doubtful that all these minerals actually formed on the Moon and not elsewhere. In deciding which minerals to include from older reports we have relied on overviews (Klein 1972, Smith 1974, Fron del 1975, El Goresy 1976, Smith & Steele 1976, Papike *et al.* 1998), as well as exchanges of information and discussions with Francis McCubbin concerning more recent reports. In compiling the list in Table 4, we included only minerals for which an indigenous lunar origin could be reasonably well established, including cohenite (Goldstein *et al.* 1976, Nazarov *et al.* 1978), hapeite ( $\text{Fe}_2\text{Si}$ ), FeSi, and  $\text{FeSi}_2$  in lunar meteorite Dhofar 280 (Anand *et al.* 2004), the latter two minerals being equivalent to naquite (Shi *et al.* 2012) and linzhiite (Li *et al.* 2012), respectively. Two potential sources of contamination of lunar samples, particularly those from the regolith, include: (1) natural phases from meteorites, *e.g.*, magnesiohornblende in fragment 24182 returned by Luna-24 (Laz'ko *et al.* 1980); and (2) natural and anthropogenic phases from terrestrial sources. In contrast to Earth, distinguishing meteoritic from lunar material is

TABLE 2. LIST OF MINERALS NOT CONSIDERED TO HAVE FORMED IN EARTH'S UPPER CONTINENTAL CRUST, AND THUS EXCLUDED FROM TABLE 1

Mineral	Formula	Rationale
Ahrensite	Fe <sub>2</sub> SiO <sub>4</sub>	Martian meteorite
Akimotoite	MgSiO <sub>3</sub>	meteorites
Allabogdanite	(Fe,Ni) <sub>2</sub> P	meteorite
Allendeite	Sc <sub>4</sub> Zr <sub>3</sub> O <sub>12</sub>	Allende meteorite
Andreyivanovite	FeCrP	Kaidun meteorite
Brezinaite	Cr <sub>3</sub> S <sub>4</sub>	meteorites
Brianite	Na <sub>2</sub> CaMg(PO <sub>4</sub> ) <sub>2</sub>	meteorites
Browneite	MnS	Zaklodzie meteorite
Buchwaldite	NaCaPO <sub>4</sub>	meteorites
Burnettite	CaVAISiO <sub>6</sub>	Allende meteorite
Buseckite	(Fe,Zn,Mn)S	Zaklodzie meteorite
Carlsbergite	CrN	meteorites; crustal occurrence doubted
Caswellsilverite	NaCrS <sub>2</sub>	meteorites
Chladniite	Na <sub>2</sub> CaMg <sub>7</sub> (PO <sub>4</sub> ) <sub>6</sub>	meteorites
Daubr�elite	FeCr <sub>2</sub> S <sub>4</sub>	meteorites
Davisite	CaScAlSiO <sub>6</sub>	meteorites
Dmitryivanovite	CaAl <sub>2</sub> O <sub>4</sub>	meteorites
Farringtonite	Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	meteorites, the Moon
Ferromerrillite	Ca <sub>9</sub> NaFe <sup>2+</sup> (PO <sub>4</sub> ) <sub>7</sub>	Martian meteorite; crustal occurrence doubted
Florenskyite	FeTiP	Kaidun meteorite
Galleiite	NaFe <sub>4</sub> (PO <sub>4</sub> ) <sub>3</sub>	meteorites
Grossmanite	CaTiAlSiO <sub>6</sub>	meteorites
Hapkeite	Fe <sub>2</sub> Si	Lunar meteorite; ureilites
Haxonite	(Fe,Ni) <sub>23</sub> C <sub>6</sub>	meteorites
Heideite	(Fe,Cr) <sub>1+x</sub> (Ti,Fe) <sub>2</sub> S <sub>4</sub>	meteorites
Hexamolybdenum	(Mo,Ru,Fe)	meteorites, crustal occurrence doubted
Hibonite-(Fe)	(Fe,Mg)Al <sub>12</sub> O <sub>19</sub>	Allende meteorite
Icosahedrite	Al <sub>63</sub> Cu <sub>24</sub> Fe <sub>13</sub>	meteoritic
Jedwabite	Fe <sub>7</sub> Ta <sub>3</sub>	natural origin doubted
Kangite	Sc <sub>2</sub> O <sub>3</sub>	Allende meteorite
Keilite	FeS	meteorites
Krinovite	Na <sub>4</sub> (Mg <sub>8</sub> Cr <sup>3+</sup> <sub>4</sub> )O <sub>4</sub> [Si <sub>12</sub> O <sub>36</sub> ]	meteorites
Krotite	CaAl <sub>2</sub> O <sub>4</sub>	NWA 1934 meteorite
Kushiroite	CaAl <sub>2</sub> SiO <sub>6</sub>	meteorites
Lingunite	NaAlSi <sub>3</sub> O <sub>8</sub>	meteorites
Linzhiite	FeSi <sub>2</sub>	Lunar meteorite, mantle xenocrysts
Majindeite	Mg <sub>2</sub> Mo <sub>3</sub> O <sub>8</sub>	Allende meteorite
Majorite	Mg <sub>3</sub> (MgSi)Si <sub>3</sub> O <sub>12</sub>	meteorites, mantle
Melliniite	(Ni,Fe) <sub>4</sub> P	meteorites
Monipite	MoNiP	Allende meteorite
Moraskoite	Na <sub>2</sub> Mg(PO <sub>4</sub> )F	Morasko meteorite
Murchisite	Cr <sub>5</sub> S <sub>6</sub>	Murchison meteorite
Nickelphosphide	Ni <sub>3</sub> P	meteorites
Nierite	Si <sub>3</sub> N <sub>4</sub>	meteorites
Niningerite	MgS	meteorites
Niobocarbide	NbC	natural origin doubted
Nuwaite	Ni <sub>6</sub> GeS <sub>2</sub>	Allende meteorite
Oldhamite	CaS	meteorites, natural origin of crustal occurrences doubted
Panethite	(Na,Ca,K) <sub>1-x</sub> (Mg,Fe <sup>2+</sup> ,Mn)PO <sub>4</sub>	meteorites
Panguite	(Ti,Al,Sc,Mg,Zr,Ca) <sub>1.8</sub> O <sub>3</sub>	Allende meteorite
Paqueite	Ca <sub>3</sub> TiSi <sub>2</sub> (Al <sub>2</sub> Ti)O <sub>14</sub>	Allende meteorite
Perryite	(Ni,Fe) <sub>8</sub> (Si,P) <sub>3</sub>	meteorites

TABLE 2. (CONTINUED)

Mineral	Formula	Rationale
Qusongite	WC	mantle xenocrysts, natural origin of crustal occurrences doubted
Ringwoodite	Mg <sub>2</sub> SiO <sub>4</sub>	meteorites, mantle
Roaldite	(Fe,Ni) <sub>4</sub> N	meteorites
Rudashevskyite	(Fe,Zn)S	Indarch meteorite
Seifertite	SiO <sub>2</sub>	meteorites
Sinoite	Si <sub>2</sub> N <sub>2</sub> O	meteorites
Stanfieldite	Ca <sub>4</sub> Mg <sub>5</sub> (PO <sub>4</sub> ) <sub>6</sub>	meteorites, natural origin of crustal occurrence doubted occurrence doubted
Tantalcarbide	TaC	natural origin doubted
Tissintite	(Ca,Na,□)AlSi <sub>2</sub> O <sub>6</sub>	Martian meteorite
Tistarite	Ti <sub>2</sub> O <sub>3</sub>	Allende meteorite
Tongbaite	Cr <sub>3</sub> C <sub>2</sub>	natural origin doubted
Tuite	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	meteorites
Wadsleyite	Mg <sub>2</sub> SiO <sub>4</sub>	meteorites, natural origin of crustal occurrences doubted
Wassonite	TiS	Yamato 691 meteorite
Xenophyllite	Na <sub>4</sub> Fe <sup>2+</sup> <sub>7</sub> (PO <sub>4</sub> ) <sub>6</sub>	Augustinovka meteorite
Xieite	FeCr <sub>2</sub> O <sub>4</sub>	Suizhou meteorite
Xifengite	Fe <sub>5</sub> Si <sub>3</sub>	Yanshan meteorite, natural origin of crustal occurrences doubted
Yagiite	NaMg <sub>2</sub> (AlMg <sub>2</sub> Si <sub>12</sub> )O <sub>30</sub>	meteorites
Yarlongite	Cr <sub>4</sub> Fe <sub>4</sub> NiC <sub>4</sub>	mantle xenocrysts
Zhanghengite	CuZn	Boxian meteorite, natural origin of crustal occurrences doubted

Note: Based on mindat.org and the IMA list as of 1 June 2014.

difficult. The frequent impacts and associated melting and breaking up of the lunar rocks have thoroughly mixed meteoritic and lunar material. Where these materials have reacted with one another, the resulting phases can be considered properly lunar, *e.g.*, stanfieldite (Shearer *et al.* 2014). As regards terrestrial contaminants, the situation in some cases is relatively unambiguous, as in the case of many hydrous minerals, *e.g.*, the “alumino-tschermakite” in sample 12021,22 (Dence *et al.* 1971) and mica, as well as almandine and tin, because neither is likely to occur on the Moon, but both are plausible contaminants. Of the four reports of amphiboles, two are plausible; *i.e.*, Ti-rich ferroargasite (Mason *et al.* 1972), although it occurs as loose grains, and magnesio-arfvedsonite (Gay *et al.* 1970), because it was “chipped from a vug” in sample 10058. However, later studies have failed to confirm these reports, and thus we have not included them in our list. Of the minerals reported more recently, we did not include the many potential minerals, such as eskolaite, Cd-rich wurtzite, baryte, bastnäsite-(Ce), fluorite, and “oxyuranobetafite” (Atencio *et al.* 2010) reported by A. V. Mokhov and colleagues (*e.g.*, Bogatikov *et al.* 2001, Mokhov *et al.* 2008, 2013) in the regolith sampled by Luna 24. Admittedly, the occurrence of

these minerals on the Moon is not inconceivable, but the reports of other phases, such as elemental boron and ytterbium in the Luna 24 regolith (Mokhov *et al.* 2011, 2013) stretches credulity, so we have decided not to include any of these reported phases in our list. Iron hydroxides have been attributed to terrestrial oxidation of lawrencite (FeCl<sub>2</sub>), but a recent study suggests a lunar origin for akaganéite as well as lawrencite in the “rusty rock” 66095 (Shearer *et al.* 2014). Calcium sulfate has been reported not only by Mokhov *et al.* (2008), but also by Righter (2013) in a lunar meteorite in which Ca sulfate occurs in a fresh fracture. Nonetheless, the possibility of terrestrial weathering of the meteorite cannot be excluded, and thus Ca sulfate is not included in our list. Overall, because of the limited number of sampling sites, the relatively few meteorites of lunar origin, and ambiguities involved in confirming primary lunar mineralogy, our list of 62 minerals (Table 4) should be considered provisional.

The most noteworthy characteristic of the list of lunar minerals is that, with the exception of hapkeite (Smith *et al.* 2008), stanfieldite, and taenite, which have only been found in meteorites; linzhiite, which has only been found as mantle xenocrysts; and yoshio-kaite, a mineral related to nepheline formed metastably

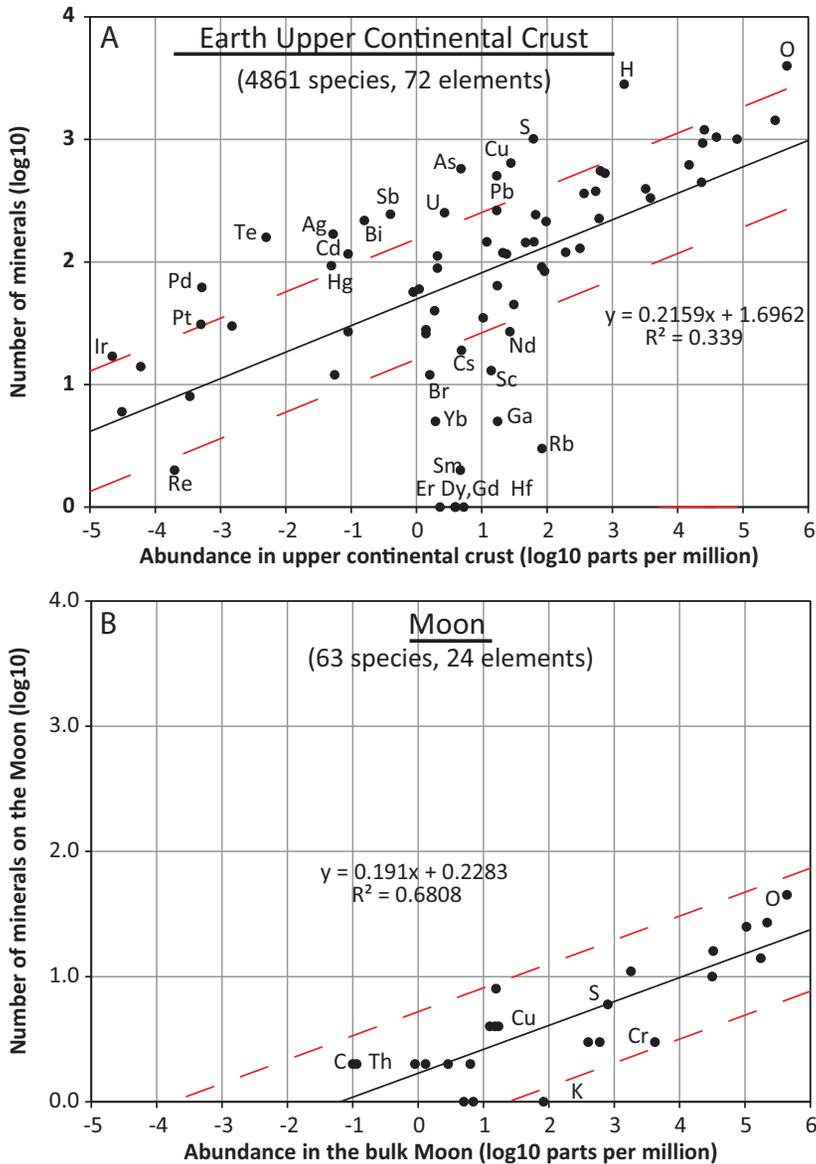


FIG. 1. (A) Number of identified minerals of terrestrial origin incorporating 72 different essential chemical elements *versus* average upper crustal abundance of the element (Table 1). The relatively low value for  $R^2$  (= 0.34) can be explained by crystal chemical factors and geochemical properties of the elements (see text). (B) Number of identified minerals of lunar origin incorporating 24 different essential chemical elements *versus* bulk Moon abundance of the element (Table 3). Red dashed lines are  $\pm 0.49$  log units above and below the trend lines (black) based on a least square fits to all the points; *i.e.*, three times more and three times less than the species indicated by trend lines.

by impact melting (Vaniman & Bish 1990), all minerals listed in Table 4 have also been found in Earth's crust (*e.g.*, Rasmussen *et al.* 2012, and references therein). These minerals include armalcolite, tranquillityite, and

pyroxferroite first discovered on the Moon; naquite (reported simply as FeSi in a fulgurite by Essene & Fisher 1986); as well as an unnamed oxide mineral, which could be vigezzite [(Ca,Ce)(Nb,Ta,Ti)<sub>2</sub>O<sub>6</sub>] or

TABLE 3. ABUNDANCE OF CHEMICAL ELEMENTS AND NUMBER OF MINERAL SPECIES ON THE MOON

Element	Abundance (ppm)*	# minerals
O	440088 <sup>†</sup>	45
Si	219000	27
Mg	175000	14
Fe	106000	25
Ca	32800	16
Al	31700	10
Cr	4200	3
Ti	1800	11
Ni	400	3
S	800 <sup>§</sup>	6
Na	600	3
K	83	1
Zr	17	4
P	15.6 <sup>†</sup>	8
Cu	15	4
Cl	12.5 <sup>‡</sup>	4
F	7 <sup>‡</sup>	1
Y	6.3	2
Zn	5	1
Ce	2.87	2
Nb	1.3	2
H	0.9 <sup>‡</sup>	2
Th	0.115	2
C	0.1 <sup>‡</sup>	2

Notes. \*Bulk moon (Taylor & McLennan 2009) unless otherwise noted; <sup>†</sup>calculated from the major oxides; <sup>§</sup>primitive bulk Moon (O'Neill 1991); <sup>†</sup>bulk silicate Moon (G.J. Taylor, pers. commun.). <sup>‡</sup>For bulk Moon (McCubbin *et al.* 2015). Mineral numbers from Table 4.

fersmite [(Ca,Ce,Na)(Nb,Ta,Ti)<sub>2</sub>(O,OH,F)<sub>6</sub>], because it has the same stoichiometry as these two terrestrial oxides.

Most likely, all the minerals listed in Table 4 originated in the lunar crust, but the possibility of a mantle source for some cannot be excluded, because major impacts may have excavated mantle material (Taylor 2009). Nonetheless, we have not attempted to use lunar crust composition as a basis for comparison, because it is heterogeneous and regionally variable (*e.g.*, Taylor 2009, Taylor & Wiczorek 2014); thus, limiting the comparison to crustal compositions would not be practical. Instead we have used models of the bulk Moon (Table 3). Of the several available models, we have selected Taylor & McLennan (2009) supplemented by O'Neill (1991), McCubbin *et al.* (2015), and C.J. Taylor (pers. commun.), instead of Warren (2005) or Taylor & Wiczorek (2014). The concentrations estimated by McCubbin *et al.* (2015) are very approximate, *i.e.*, 3 to 13 ppm H<sub>2</sub>O, 50 to 500 ppb C, and 11 to 14 ppm Cl.

Despite the relatively low mineral diversity on the Moon, the increase in number of minerals with abundance is parallel to that for Earth (Fig. 1B), but displaced nearly two log units lower, because the total diversity on the Moon is only 1% of that in Earth's upper continental crust:

$$\text{Log}(N_M) = 0.19 \text{Log}(C_M) + 0.23 \quad (R^2 = 0.68)$$

[Equation 2]

where  $C_M$  is the element's abundance in ppm in the bulk Moon and  $N_M$  is the number of lunar mineral species (all but two IMA approved) in which that element is essential (Table 3). That is, the slope in the abundance-diversity relationship expressed in Equation 1 appears to apply equally well to the Moon within the uncertainties in the data, despite the great disparity in overall diversity, whereas the intercept at  $\text{Log}(C) = 0$  differs for Earth and the Moon because of the difference in total mineral diversity.

### Meteorites

Mineral diversity of meteorites considered together has substantially exceeded 295 species; the number reached in 1997 (Rubin 1997a, 1997b), as a result of recent discoveries (*e.g.*, Ma & Krot 2014 and references cited therein). However, this diversity cannot be treated with the same approach used for Earth and the Moon because meteorites are a heterogeneous lot, being derived from numerous asteroids, Mars, and the Moon, and comprising core, mantle, and crust of these bodies, as well as pre-solar material. Nevertheless, detailed analysis of genetically related meteorite subgroups, such as the howardite-eucrite-diogenite (HED) meteorites thought to originate from the asteroid 4 Vesta (Binzel & Xu 1993, Mittlefehldt *et al.* 1998), though not considered here, might prove fruitful.

### Deviations from the Abundance—Diversity Relationship

The significant scatter in Figure 1A deserves further statistical analysis, for example using support vector machines (Bennett & Campbell 2000) and cluster analysis (Rodríguez & Laio 2014). Such analyses are in progress, but qualitative crystal chemical principles point to factors influencing why many elements lie significantly off the dominant trend defined by Equation 1, *i.e.*, by more than a factor of 3, indicated by the red dashed lines in Figure 1A. On the one hand, relatively rare elements that occur predominantly in only one oxidation state and one crystal chemical environment (*e.g.*, nearest neighbor oxygen coordination), and that readily enter into solid solutions with much more common elements, typically do not form many minerals in which that element is defined as essential. These elements thus lie well

TABLE 4. PROVISIONAL LIST OF 62 MINERALS OCCURRING IN THE MOON'S CRUST

Mineral	Formula*	Source
Akaganéite	(Fe <sup>3+</sup> , Ni <sup>2+</sup> ) <sub>8</sub> (OH, O) <sub>16</sub> Cl <sub>1.25</sub> ·nH <sub>2</sub> O	(1)
Albite	NaAlSi <sub>3</sub> O <sub>8</sub>	(2)
Anorthite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	(3)
Armalcolite	(Mg, Fe <sup>2+</sup> )Ti <sub>2</sub> O <sub>5</sub>	(3)
Augite	(Ca, Mg, Fe) <sub>2</sub> Si <sub>2</sub> O <sub>6</sub>	(3)
Baddeleyite	ZrO <sub>2</sub>	(3)
Bornite	Cu <sub>5</sub> FeS <sub>4</sub>	(3)
Chalcopyrite	CuFeS <sub>2</sub>	(3)
Chevkinite-(Ce)	Ce <sub>4</sub> (Ti, Fe <sup>2+</sup> , Fe <sup>3+</sup> ) <sub>5</sub> O <sub>8</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	(4)
Chlorapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	(5)
Chromite	FeCr <sub>2</sub> O <sub>4</sub>	(3)
Clinoenstatite	MgSiO <sub>3</sub>	(6)
Cohenite	Fe <sub>3</sub> C	(7)
Copper	Cu	(3)
Cordierite	Mg <sub>2</sub> Al <sub>4</sub> Si <sub>5</sub> O <sub>18</sub>	(8)
Corundum	Al <sub>2</sub> O <sub>3</sub>	(3)
Cristobalite	SiO <sub>2</sub>	(3)
Cubanite	CuFe <sub>2</sub> S <sub>3</sub>	(9)
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>	(3)
Enstatite	MgSiO <sub>3</sub>	(3)
Farringtonite	Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	(10)
Fayalite	Fe <sub>2</sub> SiO <sub>4</sub>	(2)
Fluorapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	(3,5)
Forsterite	Mg <sub>2</sub> SiO <sub>4</sub>	(3)
Graphite	C	(11)
Halite	NaCl	(12)
Hapkeite	Fe <sub>2</sub> Si	(13)
Hedenbergite	CaFeSi <sub>2</sub> O <sub>6</sub>	(2)
Hercynite	FeAl <sub>2</sub> O <sub>4</sub>	(3)
Hydroxylapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	(14)
Ilmenite	FeTiO <sub>3</sub>	(3)
Iron	α-Fe	(3)
Keiviite-(Y)	Y <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	(15)
K-feldspar	KAlSi <sub>3</sub> O <sub>8</sub>	(3)
Lawrencite	FeCl <sub>2</sub>	(1)
Linzhiite	FeSi <sub>2</sub>	(13)
Mackinawite	(Fe, Ni) <sub>1+x</sub> S	(3)
Magnesiochromite	MgCr <sub>2</sub> O <sub>4</sub>	(16)
Merrillite	Ca <sub>9</sub> NaMg(PO <sub>4</sub> ) <sub>7</sub>	(17)
Monazite-(Ce)	CePO <sub>4</sub>	(18)
Naquite	FeSi	(13)
"Oxycalciobetafite"	(Ca) <sub>2</sub> (Ti, Nb) <sub>2</sub> O <sub>6</sub> O	(19)
Pigeonite	(Mg, Fe, Ca)SiO <sub>3</sub>	(3)
Pyroxferroite	FeSiO <sub>3</sub>	(3)
Quartz	SiO <sub>2</sub>	(3)
Rhönite (Fe analogue)	Ca <sub>4</sub> (Fe <sup>2+</sup> <sub>10</sub> Ti <sub>2</sub> ) O <sub>4</sub> [Si <sub>8</sub> Al <sub>4</sub> O <sub>36</sub> ]	(20)
Rutile	TiO <sub>2</sub>	(3)
Schreibersite	(Fe, Ni, Cr) <sub>3</sub> P	(21)
Sphalerite	ZnS	(3)
Spinel	MgAl <sub>2</sub> O <sub>4</sub>	(8)

TABLE 4. (CONTINUED)

Mineral	Formula*	Source
Stanfieldite	Ca <sub>4</sub> Mg <sub>5</sub> (PO <sub>4</sub> ) <sub>6</sub>	(1)
Taenite	γ-(Ni, Fe)	(3)
Thorite	ThSiO <sub>4</sub>	(22)
Titanite	CaTiSiO <sub>5</sub>	(3)
Tranquillityite	Fe <sup>2+</sup> <sub>8</sub> Ti <sub>3</sub> Zr <sub>2</sub> Si <sub>3</sub> O <sub>24</sub>	(3)
Tridymite	SiO <sub>2</sub>	(3)
Troilite	FeS	(3)
Ulvöspinel	Fe <sub>2</sub> TiO <sub>4</sub>	(3)
Unnamed oxide	(Ca, Th, Y, Pb) (Nb, Ti) <sub>2</sub> O <sub>6</sub>	(23)
Yoshiokaite	Ca <sub>1-x</sub> (Al, Si) <sub>2</sub> O <sub>4</sub>	(24)
Zircon	ZrSiO <sub>4</sub>	(3)
Zirconolite	(Ca, Y)Zr(Ti, Mg, Al) <sub>2</sub> O <sub>7</sub>	(3)

Notes. \*From the IMA list except for oxycalciobetafite, rhönite (Fe analogue) and unnamed oxide.

Sources: (1) Shearer *et al.* (2014); (2) Seddio *et al.* (2013); (3) Klein (1972); Smith (1974); Frondel (1975); Smith & Steele (1976); Papike *et al.* (1998); (4) Muhliff *et al.* (2014); (5) McCubbin *et al.* (2011); (6) Ghose *et al.* (1973); (7) Goldstein *et al.* (1976); Nazarov *et al.* (1978); (8) Marvin *et al.* (1989); (9) Taylor & Williams (1973); (10) Dowty *et al.* (1974); (11) Steele *et al.* (2010); (12) Clanton *et al.* (1978); McKay & Wentworth (1992); (13) Anand *et al.* (2004); (14) Tartèse *et al.* (2014); (15) Carpenter *et al.* (2011); (16) Dymek *et al.* (1975); Shervais *et al.* (1984); Elardo *et al.* (2012); (17) Jolliff *et al.* (2006); (18) Lovering *et al.* (1974); Jolliff (1993); (19) reported as "ytrobetafite", Meyer & Yang (1988); Hinton & Meyer (1991); Atencio *et al.* (2010); (20) Treiman (2008); Grew *et al.* (2008); (21) Grieve & Plant (1973); (22) Seddio *et al.* (2012); (23) Reported as "pyrochlore" by Dymek *et al.* (1975), only Ca, Th, Nb, and Ti are considered essential; (24) Vaniman & Bish (1990).

below the general trend of Figure 1A, forming less than a third of the numbers of mineral species predicted by Equation 1. For example, Ga<sup>3+</sup> (17.5 ppm crustal abundance) usually substitutes for Al<sup>3+</sup> (8.2% crustal abundance) in octahedral coordination with oxygen. Gallium therefore typically occurs as a minor element in numerous aluminum minerals, whereas only six gallium mineral species have been approved by the IMA (two of which are sulfides and thus unlikely to occur in Al isomorphs). By contrast, Equation 1 predicts almost 100 species for Ga—a diversity that might be realized if Al were also a trace element. Similarly, Rb might be expected to form 130 or more mineral species based on its crustal abundance of 84 ppm, but it is recognized as an essential element in only three species because it readily forms solid solutions with potassium in K minerals. By the same token, Hf (5.3 ppm) follows the more abundant Zr (193 ppm), whereas the less common rare earth elements (REE), such as Dy, Er, Gd, and Sm (all <8 ppm), are usually incorporated as minor constituents of minerals with more abundant REE such

as Ce (63 ppm) and La (31 ppm), or with Y (21 ppm). Thus, crystal chemical considerations explain the limited number of species for these elements despite their crustal abundances and their common occurrence as minor or trace elements in many more species.

Conversely, 16 elements lie significantly above the general trend of Figure 1A; *i.e.*, they display at least three times more species (upper red dashed line) than would be predicted by crustal abundances alone. Included in this group are Ag, As, Bi, Cu, H, Hg, O, Pb, Pd, S, Sb, Te, and U. Oxygen could owe its diversity simply to its presence in 80% of the crustal minerals; it is unique in that it forms bonds to at least 62 of the other 72 essential elements in minerals (the exceptions being F, Cl, Au, and the platinum group elements). Each of the other elements that lies significantly above the Figure 1A trend possesses at least two of the following five chemical characteristics that might explain its above-average diversity:

(1) The element has unique crystal chemistry; *i.e.*, its combinations of ionic radii, oxidation state, and coordination number are not duplicated by any more common crustal element, so it is not easily incorporated as a minor element in other minerals. For example, tiny  $H^+$  rarely substitutes for another cation, but rather forms its own complexes as hydroxyl and water groups. Similarly,  $U^{6+}$  is not only the only hexavalent cation with ionic radius greater than 0.8 Å in seven- or eight-coordination (Shannon 1976), but it also forms the unique linear  $UO_2^{2+}$  uranyl ion, which leads to a great diversity of mineral structures (Burns 2005).

(2) The element occurs in multiple oxidation states, and thus can play multiple crystal chemical roles. Copper, for example, is found as siderophile  $Cu^0$  as in native copper (Cu), and as chalcophile or lithophile  $Cu^{1+}$  as in chalcocite ( $Cu_2S$ ) and cuprite ( $Cu_2O$ ), or  $Cu^{2+}$  as in covellite (CuS) and tenorite (CuO). Sulfur displays a similar diversity of valence:  $S^{6+}$  in sulfate,  $S^0$  in native sulfur, and  $S^{2-}$  in some sulfides, as well as complex valences in other sulfides and sulfosalts. Arsenic shows an even greater number of valence states in minerals: the native element (arsenic,  $As^0$ ), sulfides (realgar, AsS), arsenides (löllingite,  $FeAs_2$ ), arsenates [erythrite,  $Co_3(As^{4+}O_4)_2 \cdot 8H_2O$ ], and arsenites (trippkeite,  $Cu^{2+}As^{3+}_2O_4$ ). Similar considerations apply to Se, Bi, Sb, and Te, all of which, like Cu, S, and As, display an order of magnitude more mineral species than would be predicted from Equation 1.

(3) The element, though relatively rare, has efficient concentration mechanisms, resulting in significantly enhanced local abundances. Thus, hydrothermal fluids can achieve solute concentrations orders of magnitude greater than average crustal abundances for such ore-forming metals as Cu, Hg, Pb, and U.

(4) The element occurs in geochemical environments commonly associated with other rare elements, so combinatoric possibilities exist for unusual minerals of distinctive compositions. For example, massive

sulfide deposits can simultaneously concentrate Ag, Cu, and Pb, as well as the group VI chalcogenide elements (S, Se, and Te), and the Group V semi-metal elements (As, Sb, and Bi), leading to a great variety of sulfosalts minerals.

(5) Though not strictly a crystal chemical factor, all of these elements are economically important and thus their minerals have been the subject of intensive exploration and research. Consequently, rare minerals, especially those that are brilliantly colored (as with many Co, Cu, Ni, and U minerals), or that form distinctive crystals in weathered near-surface ore bodies and mine dumps, have a greater probability of being discovered and studied.

The corresponding diagram for the Moon (Fig. 1B) shows a tighter fit, perhaps because none of the anomalous elements discussed above, except S and O, are essential constituents in lunar minerals. The data for S plot close to the trend, consistent with its lunar presence in sulfide only, and thus it behaves like other elements present in a single valence state. Potassium, Cr, and Th deviate more from the trend than other elements, but still lie close to or inside the red lines that indicate threefold deviation.

In summary, given that the crystal chemical behaviors of the 72 essential mineral-forming elements are well established and will be similar on any terrestrial planet or moon comparable in size (*i.e.*, having radii in the same range as Earth and its Moon, 6378.14 and 1737.4 km, respectively), we suggest that the increase in mineral diversity with element abundance, which has a slope near 0.2 on the log-log plots in Figure 1, is a deterministic aspect of planetary mineral diversity. That nearly all the minerals confirmed as lunar are also found in Earth's upper continental crust, albeit in different proportions, could be the reason behind the similarity in slope. However, total diversity, which is reflected in how much the trend line lies above the x-axis, differs markedly between Earth's crust and the Moon. Available information undoubtedly underestimates total mineral diversity on the Moon: the 62 species listed in Table 4 are an order of magnitude less than Hazen's (2013) estimated maximum of 420 species. Nonetheless, a diversity of a few hundred species could be close to the minimum for a rocky, Earth-like planet or moon having a radius between 1000 and 10,000 km. Mineral-forming processes on the Moon are limited to igneous activity (*i.e.*, melting, crystallization, differentiation, and crystal settling), meteor impacts, and the solar wind—processes that could affect any planet or moon lacking an atmosphere and hydrosphere. In contrast, Earth and, most likely, some other planets have been subjected to other processes, all of which would increase mineral diversity. Thus, we conclude that total mineralogical diversity varies deterministically from one terrestrial planetary body to another based on the range of physical, chemical, and biological processes at play.

Christy (2015) has recently provided a similar and complementary analysis of mineral abundances in the context of “anomalous mineralogical diversity in the Periodic Table.”

#### What is the Total Potential Mineral Diversity?

Data in Table 1 suggest that many more plausible minerals might form than have been thus far described. The most common crustal rock-forming elements—silicon, aluminum, calcium, and iron—each comprises more than 2.5% of Earth’s upper continental crust and each is represented by more than 1000 known species. Accordingly, we suggest that 1000 different minerals is a minimum potential diversity for any of the 72 essential mineral-forming chemical elements; in other words, employing any of the 72 essential elements, one could readily synthesize at least 1000 different inorganic crystalline compounds incorporating that element under crustal pressure-temperature conditions and in the presence of varying combinations of other essential crustal elements. Thus we conclude that, given the significant possibilities for local concentration mechanisms and juxtaposition of unusual chemical environments in Earth-like planets, the potential exists for 1000 different stable minerals of every element. However, on any given terrestrial planet at any specific time far fewer minerals of each rare element will occur, owing to stochastic processes.

This hypothesis suggests a procedure to approximate the total number of possible mineral species. A survey of the 4933 IMA approved minerals indicates that species on average incorporate 4.70 chemical elements (a value obtained by summing the number of different elements in all 4933 IMA official mineral formulas and dividing by 4933). Thus, if each of the

72 essential mineral-forming elements is represented by 1000 potential minerals, then the approximate maximum potential crustal mineralogical diversity,  $D_{max}$ , on an Earth-like terrestrial planet is:

$$D_{max} \sim (72 \text{ elements} \times 1000 \text{ species per element}) / 4.7 \sim 15,300 \text{ species.}$$

[Equation 3]

Earth’s observed mineral diversity—4933 species as of 1 June 2014—thus represents approximately 30 percent of the total potential mineralogical diversity of an Earth-like planet.

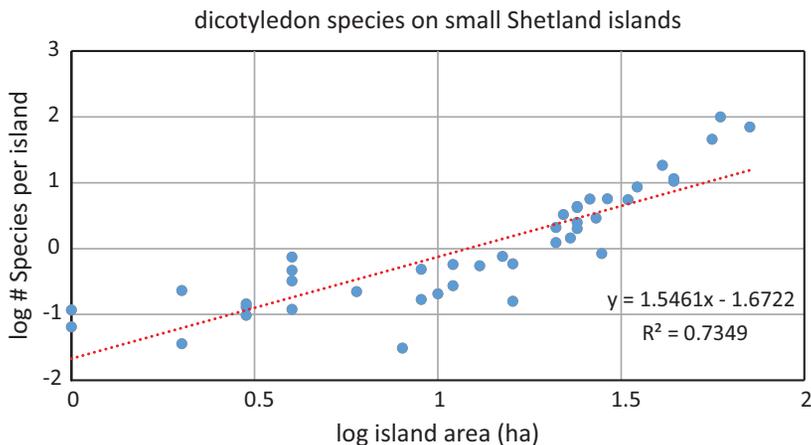
#### Island Biogeography and Mineral Diversity

The relationship between crustal abundance and numbers of species for each element (Eqs. 1 and 2; Fig. 1) bears a strong similarity to the well documented island biogeography formalism first proposed by MacArthur & Wilson (1967) and subsequently refined by many authors (Kohn & Walsh 1994, Bramson *et al.* 1996, Quammen 1996, Lomolino 2000, Hubbell 2001, Rosindell & Cornell 2009). According to this relationship, the diversity of biological species on islands reflects the area of islands (or otherwise isolated ecosystems):

$$\text{Log}(N) = a\text{Log}(A), \quad \text{[Equation 4]}$$

where  $N$  is the number of biological species (of specific taxa or in total),  $A$  is the area of the island or ecosystem, and  $a$  is a constant appropriate to the specific ecozone and taxa (Fig. 2).

The similarity of Equations 1 and 2 to Equation 4 suggests a possible analogy between the surface area of an island ecosystem (which correlates with biodiversity) and the extent of “composition space” sampled



by Earth's varied crustal environments (which correlates with mineral diversity). In each instance a greater number of species arises from enhanced combinatorial richness of the environment in which the species emerge.

If Equations 1, 2, and 4 are in some ways analogous, then it is intriguing to compare details of the diversification of minerals *versus* island biology. Ecologists have identified several factors that influence the evolution of island biodiversity, including the distance from other islands, the age or period of isolation of the island, the island's topography, habitat variability, the local climate and variability of weather patterns, the serendipitous arrival of alien species, and human interactions. Analogies of these biodiversification factors in "mineral ecology," though intriguing, have yet to be explored.

## PART II: STABILITY RELATIONSHIPS

The relationship between an element's crustal abundance and diversity of mineral species points to the critical role of compositional phase space in mineral diversification. Accordingly, the topology of phase diagrams in multi-dimensional composition space deserves further scrutiny.

## Binary Systems

Consider binary systems: Some minerals have extensive stability fields in pressure-temperature-composition ( $P$ - $T$ - $X$ ) space. For example, cinnabar ( $\text{HgS}$ ) is by far the most common mercury mineral, with more documented localities than all other Hg minerals combined (Hazen *et al.* 2012). Cinnabar and its two high-temperature  $\text{HgS}$  polymorphs, metacinnabar and hypercinnabar, are the only binary sulfides of Hg (Fig. 3a; Potter & Barnes 1978). By contrast, more than a dozen binary phases are known in the Cu-S system (Fig. 3b; Sharma & Chang 1980). Consequently, no one copper sulfide dominates the near-surface distribution of copper minerals. The H-C system provides an extreme example of a binary system with numerous competing phases. Countless thousands of hydrocarbon compounds (including 10 named mineral species, and many more undoubtedly yet to be identified) have been documented and can coexist in coal and petroleum (Selley 1985, Speight 1999). Thus, one might conclude that a single mineral phase with extensive  $P$ - $T$ - $X$  stability will suppress the mineral diversity of its incorporated elements. By contrast, a compositional system with numerous phases might display a corresponding increase in mineral diversity for those elements.

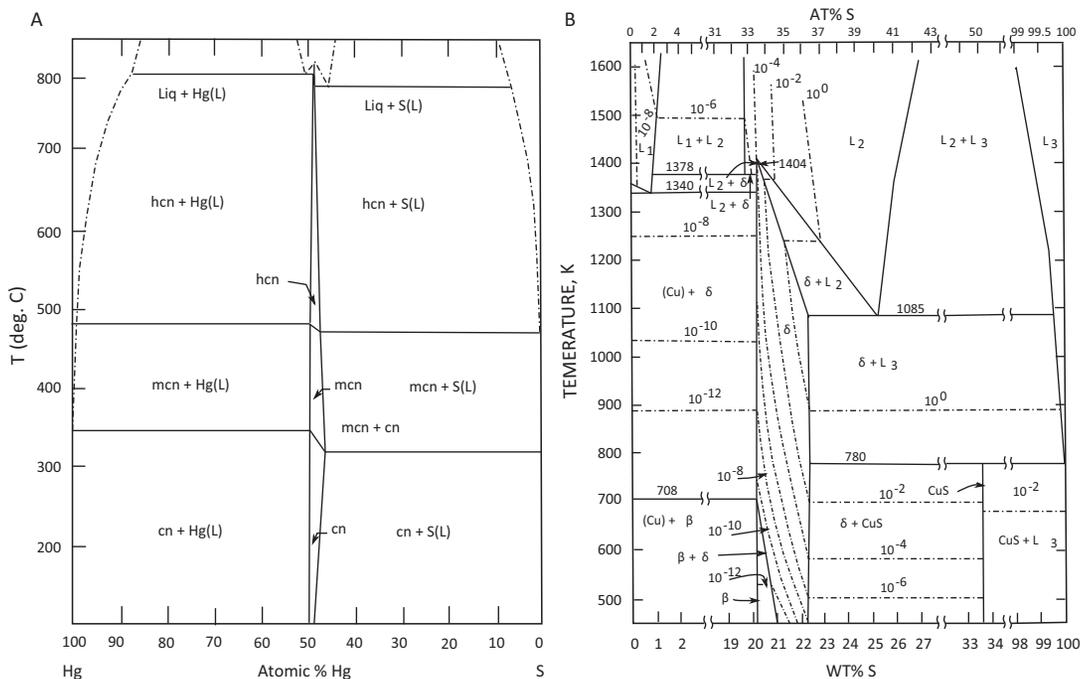


FIG. 3. Binary phases diagrams of (A) Hg-S (after Potter & Barnes 1978), and (B) Cu-S (after Sharma & Chang 1980), display contrasting numbers of mineral species. The Hg-S phase diagram is sparse, with only cinnabar ( $\text{HgS}$ ) and its two high-temperature polymorphs hypercinnabar and meta cinnabar. By contrast, the Cu-S phase diagram is relatively crowded with at least 13 binary sulfides in the Cu-S system.

Examination of the statistics of mineral occurrence reveals that this conclusion is incorrect. Both Hg and Cu, for example, lie significantly above the trend in Figure 1A. The element mercury displays an order of magnitude more phases than might be expected from its crustal abundance, despite the relative parsimony of the binary Hg–S system. Similarly, zircon ( $\text{ZrSiO}_4$ ) is by far the most common zirconium mineral with more than 4500 recorded localities—almost four times more localities than all other Zr minerals combined (based on localities recorded at mindat.org). The next most common Zr minerals—baddelyite ( $\text{ZrO}_2$ ), eudialyte  $[\text{Na}_{15}\text{Ca}_6\text{Fe}_3\text{Zr}_3\text{Si}(\text{Si}_{25}\text{O}_{73})(\text{O},\text{OH},\text{H}_2\text{O})_3(\text{Cl},\text{OH})_2]$ , and zirconolite  $[(\text{Ca},\text{Y})\text{Zr}(\text{Ti},\text{Mg},\text{Al})_2\text{O}_7]$ —have fewer than 200 recorded localities, whereas most Zr mineral species are known from only one or two localities. Nevertheless, in spite of the dominance of zircon in terms of total abundance, 121 different Zr minerals are known. That diversity is consistent with zirconium’s average crustal abundance of 190 ppm (Fig. 1A; Eq. 1).

These results point to the important role of numerous diverse “compositional niches” that are encompassed in 72-dimensional composition space. No one mineral phase or group of phases can occupy more than a small “volume” of this multi-dimensional space. Thus, we estimate that perhaps 1000 potential Zr minerals occur in compositional regimes away from the zircon-dominated Zr–Si–O system. We conclude, therefore, that the occurrence of one or more extremely stable phases of an element is not sufficient to suppress mineral diversity for that element.

#### *The Biosphere and Enhancement of Earth’s Compositional Space*

Hazen *et al.* (2008) suggested that the single most important factor in Earth’s mineral diversification was the evolution of oxygenic photosynthesis. Prior to Earth’s global oxygenation, shallow subsurface environments were effectively buffered by the ubiquitous presence of ferrous iron in both oceans and soils—a circumstance that constrained Hadean and Archean shallow subsurface  $f_{\text{O}_2}$  to be close to the magnetite-hematite buffer ( $f_{\text{O}_2} \sim 10^{-72}$  at STP; Sverjensky & Lee 2010, Hazen *et al.* 2012, 2013a, Golden *et al.* 2013). The complete range of  $f_{\text{O}_2}$  in shallow subsurface environments probably extended from the iron-wüstite buffer (for example, at sites of iron-rich meteorite impacts) with  $f_{\text{O}_2} \sim 10^{-88}$  (Johnson *et al.* 1992), to several log units above the magnetite-hematite buffer—a maximum range of perhaps 30 log units in  $f_{\text{O}_2}$  ( $-90 < \log[f_{\text{O}_2}] < -60$ ) in all near-surface Hadean and early Archean environments. Thus, for example, minerals incorporating such relatively oxidized cations as  $\text{Cu}^{2+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Ni}^{3+}$ , and  $\text{U}^{6+}$  would not have been stable.

The advent of oxygenic photosynthesis and the rise of atmospheric oxygen to  $\sim 0.2$  bar in the Neopro-

terozoic Era (Canfield 2014, Lyons *et al.* 2014) expanded the near-surface range of oxygen fugacity to  $-90 < \log[f_{\text{O}_2}] < 1$ . The biosphere, through the creation of an extreme redox gradient at Earth’s surface, in effect caused a tripling of oxygen fugacity space and led to the formation of thousands of new mineral species. Because oxygen is the most abundant crustal element, present in more than 80% of known minerals, it is perhaps not surprising that life thus led to a tripling of the number of mineral species (Hazen *et al.* 2008). The diversification of minerals subsequent to the Great Oxidation Event underscores the importance of the accessibility of multi-dimensional composition space in determining the total mineral diversity.

#### *Mineralogical Habitability and Habitable Zones*

The concepts of “habitability” and the “habitable zone” are recurrent themes in astrobiological research. On the one hand, the “circumstellar habitable zone” is a radially symmetrical, toroidal volume of a star system in which a planet or moon with sufficient atmospheric pressure can support liquid water—a world where life could potentially arise and evolve at or near planetary surfaces (Huggett 1995, Brownlee & Ward 2004, Kasting 2010, Kopparapu 2013). A star’s habitable zone depends primarily on the stellar radiation flux, including the flux of harmful ultraviolet radiation, parameters that are significantly influenced by the type of star and distance from its surface, and thus can potentially be evaluated for distant stellar systems. On the other hand, “habitability” may also refer to the generative potential for life to emerge and evolve on a specific planet or moon. Thus, for example, Earth’s Moon is clearly within our Solar System’s habitable zone but, lacking an atmosphere and liquid water, is uninhabitable. Venus possesses an atmosphere and is also arguably within the Sun’s habitable zone, but is not now a habitable planet owing to its hot, dry surface conditions. Thus, numerous factors influence a specific planet’s habitability, for example: (1) the planet’s composition, especially its near-surface volatile content and atmospheric composition; (2) the presence of liquid water; (3) the planet’s orbital parameters, notably its eccentricity; (4) the planet’s rotation parameters, including its inclination and temporal variations that might affect climate and weather; (5) the flux of large impactors; and (6) geodynamic cycling between crust and mantle, which sustains geochemical gradients that can be exploited by organisms.

Concepts of “habitable zones” and “habitability,” to the extent that they might reflect mineral-forming regimes of pressure, temperature, and composition, play important roles in the observed diversity of minerals. Thus, for example, one can point to “habitable zones” and “habitability” for each mineral in a star system—concepts that simply reflect *P-T-X* stability considerations based on phase equilibria. However,

casting mineral occurrence in the context of habitable zones serves to classify planets in their entireties as worlds where certain minerals may or may not form. Thus, with respect to clay minerals the near-surface environments of Mars and Earth are both habitable, as well as within the habitable zones (Hazen *et al.* 2013b). By contrast, the Moon and Mercury appear to be too dry, and Venus too hot, to be habitable for clay minerals, and thus it is not surprising that no clay mineral has been convincingly reported in lunar rocks (*e.g.*, Frondel 1975).

Many theories for life's origins rely on specific minerals, for example as catalysts for organic synthesis, as protective environments for otherwise vulnerable biomolecules, or as templates for molecules to organize (*e.g.*, Hazen 2006, Cleaves *et al.* 2012, Furukawa *et al.* 2013, and references therein). To the extent that a mineral species is essential for the origins of life, a stellar system's habitable zone for life must be a subset of the habitable zone for that mineral species. Indeed, life can only arise within the habitable zones of all minerals essential to life's origins. Furthermore, the specific planet or moon under consideration must be habitable for those minerals, as well.

### PART III: MINERAL FREQUENCY DISTRIBUTION RELATIONSHIPS

To what extent is the distribution of observed mineral species a matter of necessity *versus* chance? Statistical methods that characterize distribution relationships can provide insight regarding the similarities and differences between Earth's near-surface mineral diversity as observed today, *versus* alternative scenarios—for example, Earth's prior geological periods, a hypothetical “replaying” of Earth history, or mineral occurrences on other Earth-like planets.

#### *Large Number of Rare Event (LNRE) Distributions*

This inquiry is analogous to studies of the frequency distribution of words to compare and contrast unsigned texts with those of known authorship. In a typical manuscript a few words are used many times (“a”, “and”, and “the”, for example), whereas many words are used only once or twice. Any given author tends to produce works with similar idiosyncratic word and phrase distributions (Mosteller & Wallace 1964, Harvey 1970, Baayen 2001, Stamatatos 2009). Thus, one can evaluate claims of authorship through statistical analysis of word frequency distributions. Such distinctive frequency distributions, which differ, for example, from Zipf's Law and related power law relationships, are known as Large Number of Rare Event (LNRE) distributions because they are characterized by the occurrence of many words with very

low probabilities (*e.g.*, Baayen 2001, Evert 2004, Evert & Baron 2008).

Earth's observed locality frequency distribution for minerals follows a distinctive pattern analogous to words in a document: A few minerals are known from tens of thousands of localities (quartz, calcite, and pyrite, for example), whereas more than a third of all mineral species are known from only one or two localities. Thus, LNRE analysis can be adapted to the study of mineral distributions and applied to evaluating the likely similarity of an alternate Earth (*i.e.*, a planet with the same “mineral authorship”) *versus* terrestrial planets that differ in initial conditions (*i.e.*, varied mineral authorships). A more comprehensive treatment of this approach to characterizing mineral distributions is forthcoming (Hystad *et al.*, in press); here we summarize our results.

We employed mindat.org (data as of 1 February 2014) as a source of 652,856 discrete combinations for 4831 mineral species and their localities—data that constitute our sample size. Despite significant geographical biases, as well as the under-reporting of localities for the most common rock-forming minerals and other potential deficiencies in this data set (see above and Grew & Hazen 2014), we conclude that the total number of species-locality data is sufficiently large, and the deficiencies sufficiently small, to justify statistical treatment of these species-locality systematics.

Consider a distribution of mineral species on Earth (analogous to the distribution of words in a text). The total number of unique combinations of a mineral species and a locality is  $N = 652,856$  (analogous to the number of words in a text); the number of different mineral species known on Earth is  $V(N) = 4831$  (analogous to the number of different words in the text); and  $V(m,N)$  is the number of minerals occurring at exactly  $m$  localities (analogous to the number of words occurring  $m$  times in the text). Table 5 lists  $V(m,N)$  for  $m \leq 15$ . Thus, 1062 minerals (22.0% of all species) are known from only one locality, whereas an additional 569 minerals (11.8% of all species) are known from exactly two localities (Fig. 4).

These values conform to a generalized inverse Gauss-Poisson distribution. We employed the R-package, zipfR (Evert & Baron 2008). Our LNRE model employs a Sichel's generalized inverse Gauss-Poisson (GIGP) structural type distribution, which fit well to our observed mineral-locality distribution. We estimated parameters by minimization with the Nelder-Mead algorithm; our simplified version of the multivariate chi-squared test for goodness-of-fit employed the first 11 spectral elements. Our parameters are  $\gamma = -0.4185485$ ,  $b = 0:01317403$ , and  $Z = 70.46155$ , with  $X^2 = 10.35823$ ,  $df = 13$ , and  $p$ -value = 0.6644109. Figure 4 shows the frequency spectrum for observed and modeled values, using Sichel's model for  $m \leq 15$ ; Figure 5 shows the observed cumulative probability *versus* number of localities for  $m \leq 15$ ; and Figure 6 shows the

TABLE 5. NUMBERS AND PERCENTAGES OF 4831 IMA APPROVED MINERALS\* THAT ARE FOUND AT 15 LOCALITIES OR LESS

# Localities	# Minerals	Probability	Cumulative Probability
1	1062	0.220	0.220
2	569	0.118	0.338
3	401	0.083	0.421
4	289	0.060	0.480
5	208	0.043	0.523
6	157	0.032	0.556
7	137	0.028	0.584
8	118	0.024	0.609
9	92	0.019	0.628
10	87	0.018	0.646
11	66	0.014	0.659
12	64	0.013	0.673
13	59	0.012	0.685
14	52	0.011	0.696
15	44	0.009	0.705

Note: More than two-thirds of all known minerals are recorded at 15 or fewer localities. This distribution is characteristic of a Large Number of Rare Event (LNRE) distribution (e.g., Baayen 2001). (As recorded at mindat.org; data as of 1 June 2014).

\*According to ruff.info/ima.

frequency spectrum for all observed minerals. Note that that curves in Figures 4, 5, and 6 depend almost exclusively on the distribution of the rarest minerals found at 15 or fewer localities (these minerals represent more than two-thirds of all documented mineral species). Thus, the severe under-reporting of localities for the most common rock-forming minerals by mindat.org does not significantly affect our LNRE distribution model.

LNRE distributions applied to lexical studies are recognized in part by the ratio of the number of words occurring only one time  $[V(1,N)]$  versus the total vocabulary size  $[V(N)]$ . It is somewhat counterintuitive that above a critical sample size  $[V(1,N)/V(N)]$  decreases as  $[V(N)]$  increases, as illustrated in Figure 7. To underscore this point, consider locality distributions of mineral species: more than 35 percent of 112 Be minerals are known from only one locality (Grew & Hazen 2014), whereas only 22 percent of all 4831 species are recorded from one locality.

#### *How Many Minerals Exist on Earth Today?*

In this study we wish to predict how similar or different a mineral distribution might be on an alternative Earth. Such a prediction is facilitated by the predictive power of the LNRE model, which points to the probable existence on Earth today of more than

1500 as yet undiscovered mineral species. Figure 7 illustrates the relationship between newly reported mineral-locality data and likely new mineral species. As the amount of data increases, new minerals are likely to be discovered and reported at a predictable rate—a feature represented in the monotonically increasing upper curve in Figure 7. This curve asymptotically approaches a value of 6394, which is the predicted total number of distinct mineral species on Earth today. This analysis suggests that 1563 mineral species are yet to be discovered, assuming that new minerals are discovered by the application of current sampling and analytical techniques. Note that the introduction of new techniques, for example, the widespread application of transmission electron microscopy to identify nano-phase minerals (e.g., Ma *et al.* 2014, Ma & Krot 2014), could result in a significant increase in this value.

#### *How different would Earth's mineralogy be if we replayed the tape?*

Our LNRE distribution model facilitates prediction of the probable similarities and differences of a resampling of an identical Earth-like planet that also holds the exact same set of 6394 mineral species that are extrapolated to exist on Earth today. If one were to “replay the tape” and document the first 4831 (of 6394) minerals to be discovered, our model predicts that almost all of the minerals known from four or more localities (*i.e.*, 2799 species or 58%) are highly probable to occur again. However, the appearances of the rarest minerals on Earth today—those with only one or two known localities—are less certain. If the total number of possible species is restricted to the estimated 6394 on Earth today, then a replaying of the tape is predicted to result in 4164 species (86.3%) that are the same on both worlds, but 662 of those mineral species (13.7%) are predicted to differ from species known today (Hystad *et al.*, in press). Thus, a significant fraction of Earth's mineral diversity appears to be a frozen accident.

This estimate represents the extreme lower bound of the expected difference between today's mineral distribution and an alternative Earth-like scenario for several reasons. First, this estimate assumes that the two worlds under comparison are identical in every respect with regard to initial crustal composition and mineral-forming processes, including identical biological influences such as the Great Oxidation Event and the rise of the terrestrial biosphere (Hazen *et al.* 2008). However, studies of planetary stoichiometry (see Part IV below) suggest that bulk compositions of different terrestrial bodies may differ significantly. Any variations in the initial parameters will result in additional differences in total mineral diversity, as well as the specific frequency distribution of those minerals.

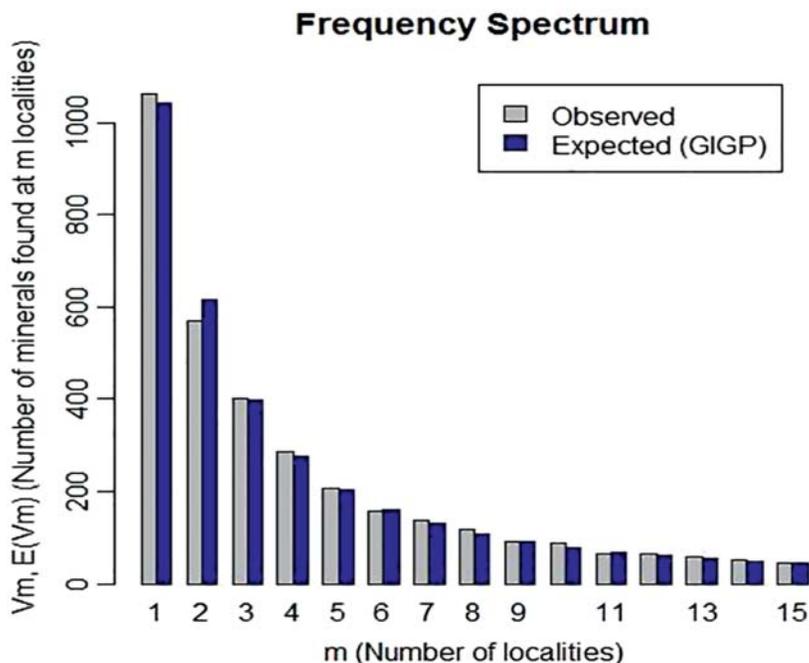


FIG. 4. Observed (grey) and predicted (black) frequency spectrum for mineral distributions. The horizontal scale indicates the number of different localities,  $m$ , at which a mineral is known. The vertical scale indicates the number of different mineral species that are known from that number of localities. Thus, 1062 minerals are known from only 1 locality, whereas 569 minerals are known from only 2 localities. The observed frequencies are in close agreement with those predicted by the large number of rare event (LNRE) distribution model (Hystad *et al.*, in press).

Our estimate of the difference between Earth and other worlds is also too low because our model at present is unable to factor in the numerous plausible minerals that might occur at some time on an Earth-like planet, but that are not in the presumed set of 6394 species on Earth today. This situation is analogous to the difficulty of extrapolating the total potential vocabulary for all books from the word distribution in a single book by a single author. Thus, the predicted number of 6394 mineral species present on Earth today is much smaller than our independent estimate above of >15,300 *plausible* minerals (the complete “mineral vocabulary”) that might occur collectively on all terrestrial planets and moons (Eq. 3).

Most of these estimated >15,300 plausible minerals correspond to unusual chemical and physical environments, some of which are much more likely than others. Thus, some of the “missing” minerals might occur on more than 50% of all Earth-like planets, whereas other phases might occur only once in a million planets. The possible distribution of these potential minerals remains a topic for further study. Nevertheless, we suggest that any replaying of the tape of Earth’s mineralogy would introduce many new rare species that are among the plausible >15,300 species, but are not included in the

presumed list of 6394 minerals on Earth today. Consequently, were we to sample the first 4831 species on another Earth-like planet, significantly more than the calculated 662 species would differ from those of today. Given the combinatorial richness of plausible mineral chemistries, we suggest that any replaying of Earth history would result in at least a quarter of all minerals—more than 1200 species—different from species known on Earth today. Furthermore, given that many of these species are rare and would be observed on fewer than half of Earth-like planets, we postulate that the chances of another terrestrial planet or moon having the identical combination of mineral species found on Earth is less than 1 in  $2^{1000} \sim 10^{300}$ .

Present estimates suggest that the universe holds on the order of  $10^{11}$  galaxies, each with on the order of  $10^{11}$  stars (John Chambers, pers. commun.; Alycia Weinberger, pers. commun.). Even if every star has a companion terrestrial planet or moon, the resulting  $10^{22}$  terrestrial worlds are hundreds of orders of magnitude fewer than the estimated combinatorial richness of terrestrial worlds. We therefore conclude that Earth is mineralogically unique, and that chance must play a significant role in the details of the evolving mineral diversity of all Earth-like planets.

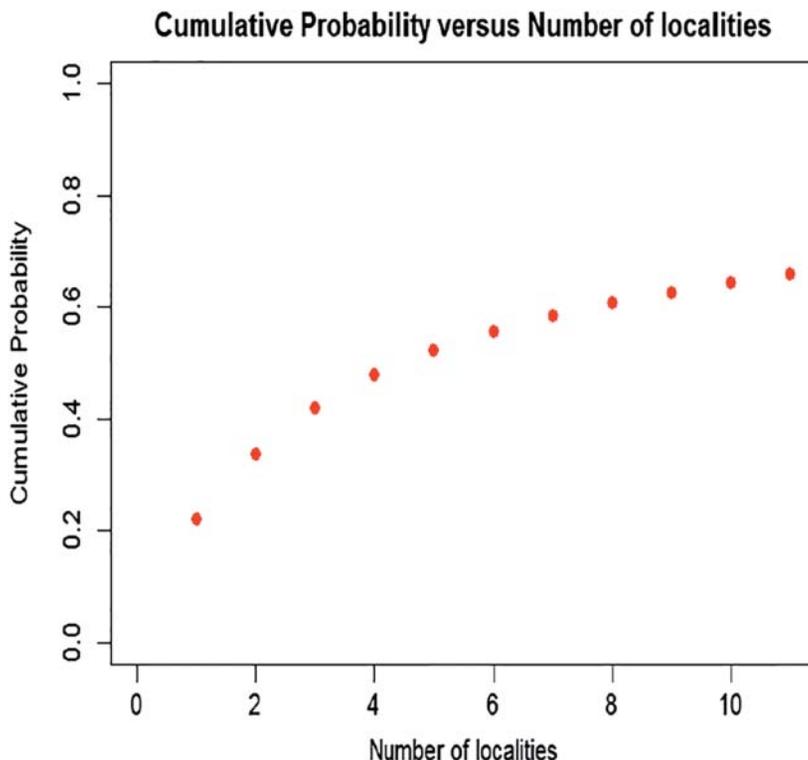


FIG. 5. Cumulative probability of a mineral species occurring *versus* the total number of localities for the mineral. For example, the probability that a mineral is found at only one locality is 22.0%, whereas the probability that it is found at 10 or fewer locations is 64.6%. Most mineral species are known from five or fewer localities.

#### PART IV: STELLAR AND PLANETARY STOICHIOMETRY

##### *Stellar Stoichiometry*

In what ways might the details of mineral evolution differ on Earth-like planets in other star systems? The analysis above suggests that the bulk composition of a planet, as well as ranges of varied near-surface composition space, will play significant roles. Furthermore, even given a planet identical to Earth in size and composition, with near identical distributions of common rock-forming minerals, chance events will lead to significant differences in the identities of rare minerals. We can expect even greater differences on planets and moons with different initial compositional and orbital parameters.

A recent and growing literature on “stellar stoichiometry,” based on the quantitative spectroscopic analysis of star compositions, reveals that some stars differ significantly from the Sun in their total and relative abundances of rock-forming elements. These differences arise both as a consequence of differing

initial “metallicity,” which is defined by the abundance of elements heavier than He, and subsequent processing by nucleosynthesis within the star. Though typically constituting only ~1.5% of a star’s mass, the elements with  $Z > 2$  play an essential role in the origins and evolution of terrestrial planets.

Young *et al.* (2014) summarized the findings of several observational astronomy groups engaged in quantitative spectroscopic measurements of stars to determine element abundances and ratios—an effort known as “stellar stoichiometry.” They concluded that stellar concentrations and relative amounts of such key elements as Al, C, Ca, Mg, Na, O, and Si may differ by factors of at least two compared to the Sun. Significantly, elemental abundances do not scale with Fe in stars, for example, in such critical stellar atomic ratios as Fe/Mg, Fe/O, Mg/Si, and C/O (Bond *et al.* 2010, Delgado-Mena *et al.* 2010, Nissen 2013).

Stellar stoichiometries are reported as ratios relative to the Sun. Thus, for example, Fe/H of a star is given as:

$$[\text{Fe}/\text{H}]_{\text{star}} = \log_{10}[(\text{Fe}/\text{H})_{\text{star}}/(\text{Fe}/\text{H})_{\text{sun}}] \quad [\text{Equation 5}]$$

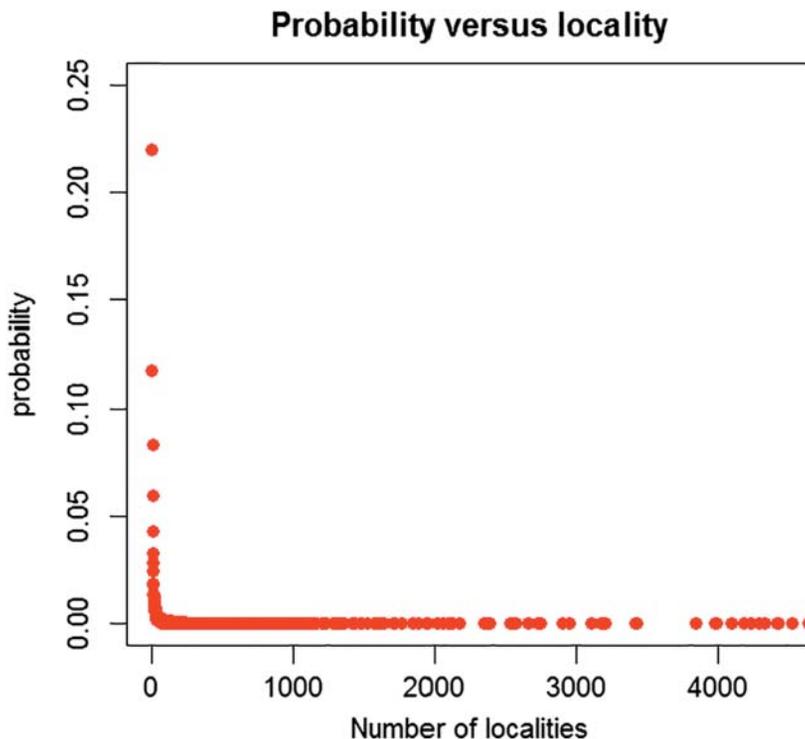


FIG. 6. The mineral frequency distribution plots each mineral's rank *versus* the number of recorded localities for 4831 mineral species (data from mindat.org as of 1 February 2014). The mineral species with the highest frequency (quartz with approximately 45,000 reported localities) is ranked number 1. By contrast, 22% of mineral species have been found at only one locality, while more than half of all mineral species are found at five or fewer localities. This pattern is an example of a Large Number of Rare Event (LNRE) distribution (*e.g.*, Baayen 2001), because it is characterized by the occurrence of many mineral species with few mineral localities.

Because Fe is the most easily measured metal in a star, and abundances of other elements are often assumed to scale roughly with Fe,  $[\text{Fe}/\text{H}]_{\text{star}}$  is commonly employed to define a star's metallicity. Observed values of  $[\text{Fe}/\text{H}]_{\text{star}}$  range from  $-6$  (*i.e.*, low-iron stars with a millionth of the Sun's iron concentration) to  $>1$  (metal-rich stars with 10 times or more iron than the Sun).

Results from the analysis of more than 3000 nearby stars (Hinkel 2012) reveal that element ratios also vary significantly from those of the Sun. Thus, for example, while C/O for most stars is less than 1 (Delgado-Mena *et al.* 2010), and may be close to 0.5 in stars like the Sun (Lodders 2010), some carbon-rich stars have C/O  $> 1$  (Madhusudhan *et al.* 2011). Similarly, Mg/Si is observed to vary from 0.8 to 2.0 (Bond *et al.* 2010) compared to 1.2 for the Sun (Lodders 2010). Such studies are still in their infancy, and discoveries of more extreme deviations from stellar stoichiometry are likely to emerge in the near future.

### Planetary Stoichiometry

These findings of significant differences in elemental abundances and ratios of stars imply that the bulk compositions of Earth-like terrestrial planets may also differ significantly from those of Earth (Bond *et al.* 2010, Carter-Bond *et al.* 2012). However, stellar (and, by extension, bulk nebular) composition is only the first of three major factors that influence a planet's near-surface composition; evolutionary processes in nebulas and differentiation of planets also play key roles. Thus, a strict 1-to-1 correlation between the compositions of stars and their planets does not obtain because of extreme fractionation processes in evolving stellar nebulas (Desch 2007, Chambers 2010a, 2010b). The ability to infer both mass and radius of exoplanets (Seager *et al.* 2007, Charbonneau *et al.* 2009, Queloz *et al.* 2009) reveals density and thus constrains relative amounts of ice, rock, and iron metal, though density alone cannot uniquely define planetary compositions. Nevertheless, density measurements by Kaltenegger *et al.* (2013)

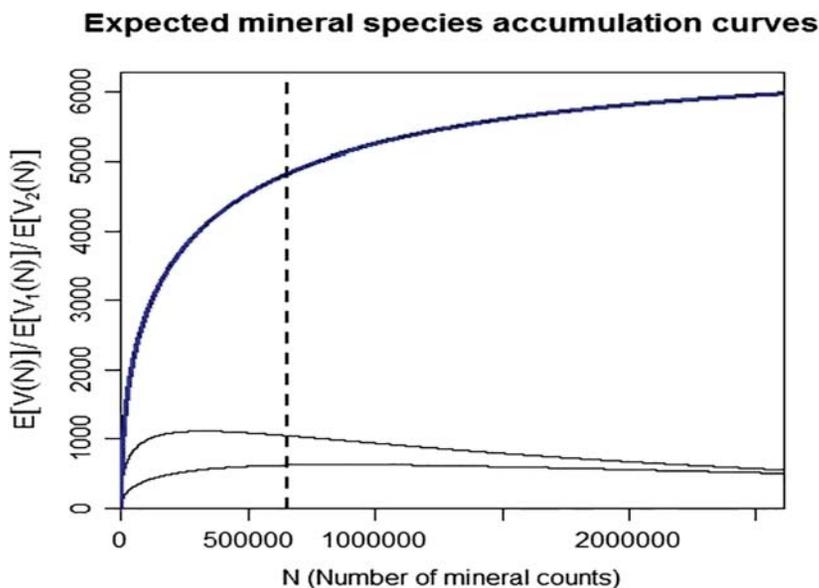


FIG. 7. The LNRE model leads to predictions of the expected increase in the number of identified mineral species (upper curve). The 4831 known mineral species represent 652,856 mineral-locality pairs, as reported by mindat.org (as of 1 February 2014; vertical dashed line). As more mineral locality data are added, the number of known species is predicted to increase. This model predicts that a total of 6394 mineral species exist, assuming that current sampling and analytical procedures are employed to identify new minerals. The lower two curves are the expected numbers of mineral species reported from only one and from exactly two localities—numbers that are predicted to vary as more mineral-locality data are added. Note that as the number of mineral-locality data increase, the numbers of species known from only one or two localities are predicted to decrease.

suggest that planet Kepler 11b has ice > rock, whereas planet CoRoT-7b has Fe metal > rock. Furthermore, discoveries by the *Kepler* mission suggest that the standard model for planetary formation by core accretion, which explained every major feature in our Solar System, may not be applicable to many other systems (Finkbeiner 2014), thereby introducing additional ambiguity in relating star and planet compositions.

The roles of evolutionary processes in nebulas and planetary differentiation are underscored in a comparison (Table 6) of solar system abundances of non-volatile elements based on abundances in CI chondrites (Lodders 2010), abundances in Earth's upper continental crust (Wedepohl 1995, Rudnick & Gao 2005), and modeled abundances in the bulk Moon (Taylor & McLennan 2009). One striking difference between the solar system as a whole and Earth is the volatile loss of carbon, which gives rise to a C/O ratio of 0.007 in Earth's upper continental crust, compared to 0.076 in the solar system. By contrast, bulk Earth retains refractory magnesium and silicon, but Mg is depleted in Earth's upper continental crust (Mg/Si = 0.048) compared to the solar system (Mg/Si = 0.895) and bulk Moon (Mg/Si = 0.799) because of efficient Mg fractionation into Earth's mantle (Mg/Si = 1.3; McDonough & Sun 1995). Similarly, formation of

Earth's core and sequestration of iron leads to a crustal Fe/Si ratio of 0.126, compared to 1.729 in the solar system. By contrast, the bulk Moon Fe/Si ratio of 0.484 implies that Fe was largely sequestered from the Moon as a whole, leaving a small core. Differences in element ratios between Earth's upper continental crust and the bulk Moon are, in most cases, reflected in ratios of mineral species for these elements; *e.g.*, the ratio of minerals containing essential Ca to minerals containing essential Mg in Earth's crust is twice the corresponding ratio on the Moon, consistent with Ca/Mg being much higher in Earth's crust than on the Moon. In summary, the comparison in Table 6 implies that the compositions of terrestrial planets and moons, particularly crustal compositions, differ significantly from one another and from the starting composition, generally thought to have been that of CI chondrites in our solar system, and these differences find expression in the minerals found. Work in progress will extend these concepts to the bulk compositions of Mercury, Mars, and asteroids.

#### *Implications of Planetary Stoichiometry*

Planetary stoichiometry has a major influence on a planet's behavior, including its near-surface mineral

TABLE 6. COMPARISON OF ELEMENT ABUNDANCES AND RATIOS FOR THE SOLAR SYSTEM, EARTH'S UPPER CONTINENTAL CRUST, AND BULK MOON

Element	CI chondrite	Earth's Crust	Bulk Moon
Composition (ppm)			
O	459,000	472,000	440,088
C	34,800	3240	0.1
Na	4990	24,259	378
Mg	95,800	14,955	175,000
Al	8500	81,505	31,700
Si	107,000	31,312	21,900
Ca	9220	25,657	32,800
Fe	185,000	39,176	106,000
Element ratio			
Mg/Si	0.895	0.048	0.799
Fe/Si	1.729	0.126	0.484
Fe/Mg	1.931	2.620	0.606
Ca/Mg	0.096	1.716	0.187
Fe/O	0.403	0.083	0.241
C/O	0.076	0.007	$2 \times 10^{-7}$
Na/Al	0.587	0.298	0.019
Ratio of predicted numbers of mineral species			
Mg/Si	—	0.43	0.52
Fe/Si	—	0.73	0.93
Fe/Mg	—	1.68	1.79
Ca/Mg	—	1.93	1.14
Fe/O	—	0.26	0.56
Na/Al	—	0.93	0.30

Notes: CI chondrite as representative of solar system abundances of non-volatile elements (Lodders 2010); Earth's upper continental crust (Rudnick & Gao 2005; except C from Wedepohl 1995); and bulk Moon (Taylor & McLennan 2009) except for O and C (Table 3). Mineral ratios are calculated from the number of minerals for an element given in Tables 1 and 3.

evolution and ecology. Bulk composition plays a dominant role in such planetary-scale processes as the size of the metal core relative to the silicate mantle, planetary oxidation and thus mantle Fe/Mg, the extent of radiogenic heating and consequent heat flow, convection dynamics, and crustal evolution.

A key factor in Earth's crustal evolution is the production of buoyant melts—a circumstance that may not obtain under all plausible upper mantle conditions. For example, Stolper and colleagues (Stolper *et al.* 1981, Agee & Walker 1988, Rigden *et al.* 1988) posited that the greater compressibility of basaltic melts compared to mantle minerals might result in cases where initial melts are denser than their host rocks. Under an extreme scenario, production of buoyant silicate melts and associated volcanism might be significantly suppressed. For example, a planet with a mantle Mg/Si  $\sim 2$  (compared to  $\sim 1.3$  for Earth) would result in an upper mantle mineralogy dominated by olivine, which produces a melt more iron-rich, and thus denser, than its host rock. Alternatively, in the case of a mantle with Mg/Si  $\sim 0.5$ , initial Si-rich melts will display

high viscosity and thus may not easily rise through the mantle to form crustal rocks.

Elkins-Tanton (2012, 2013) has emphasized the important role of magma ocean formation and solidification in the evolution and habitability of terrestrial planetary crusts. It is likely, for example, that some planets in close proximity to their star, and thus with significant positive net heat flux, may require hundreds of millions of years for their magma oceans to cool (Hamano *et al.* 2013). These hot planets likely lose their crustal volatiles before complete solidification of a magma ocean, and thus never develop a near-surface hydrosphere and such associated mineral-forming processes as hydrous weathering, soil formation, and, most significantly, a biosphere, all of which contribute to mineral diversification.

Earth's magma ocean, by contrast, likely cooled in a few million years (Abe 1997, Zahnle *et al.* 1988), with corresponding retention of volatiles and rapid development of a dynamic hydrosphere. In this regard, the distribution of volatiles and the nature of near-surface fluids, notably in the system C-O-H, play dominant

roles in crustal dynamics and evolution (Dasgupta 2013, Jones *et al.* 2013, Manning *et al.* 2013).

On Earth, the subduction of hydrated basalt results in partial melting to produce less dense granitic melt, which rises to form continents. Most of Earth's initial mineralogical diversity (as many as 1500 mineral species; Hazen *et al.* 2008) is thus a consequence of crust formation and significant partitioning of incompatible elements into crust-forming fluids. If, however, an initial melt is denser than its host rocks then formation of crust and continents, and associated crustal mineralization, would be severely restricted. Plate tectonics, volcanism, and near-surface fluid-rock interactions might be significantly suppressed, with consequent restrictions on the origins of both minerals and, ultimately, the origin and evolution of life.

### SUMMARY

The occurrence of minerals on terrestrial planets and moons arises through a combination of deterministic and stochastic processes. Among the most important deterministic factors are:

- *Element abundances:* More common elements generally give rise to a greater number of mineral species, according to the relationship for Earth and the Moon, respectively:

$$\text{Log}(N_E) = 0.22 \text{Log}(C_E) + 1.70 \quad (R^2 = 0.34)$$

$$\text{Log}(N_M) = 0.19 \text{Log}(C_M) + 0.23 \quad (R^2 = 0.68)$$

The similarity in slope implies that the minerals of the most abundant elements, including O, Si, Mg, Ca, Al, and Fe, dominate the near-surface environments of Earth and the Moon, and could do likewise on other terrestrial planets and moons.

- *Crystal chemistry:* Rarer elements that mimic more common elements produce fewer mineral species than predicted by the relationship, whereas elements with multiple and/or unique crystal chemical behaviors produce more mineral species than predicted.
- *Phase equilibria:* Numerous “compositional niches” are encompassed in 72-dimensional composition space. No one mineral phase or group of phases can occupy more than a small “volume” of this multi-dimensional space, which may incorporate more than 15,000 plausible crustal minerals.
- *Mineral frequency distributions:* The frequency of mineral occurrences on Earth conforms to a large number of rare event (LNRE) distribution. Thus, a few common rock-forming minerals

will be dominant in terms of crustal volume on any terrestrial planet or moon.

- *Planetary stoichiometry:* Planets with significantly different ratios of major elements than Earth will likely also display significantly different distributions of rock-forming minerals. Different bulk mineralogy can lead to dramatically different planetary-scale dynamics, as well.

Superimposed on these deterministic aspects of planetary mineralogy are important stochastic processes. More than a third of Earth's mineral diversity arises from species known from only one or two localities—a circumstance suggesting that rare events and frozen accidents play a nontrivial role in Earth's near-surface mineralogy. A few hundred common rock-forming minerals dominate Earth's crustal volume but, like raisins in a muffin, much of the mineralogical interest lies in widely dispersed novelties, which arise by chance physical and chemical circumstances. The combinatorial richness of thousands of rare species ensures that Earth is mineralogically unique.

### CONCLUSIONS

The consideration of mineral distributions through space and time points to new avenues of research—a pursuit that we characterize as “mineral ecology.” Like biological studies of ecosystems, our goal is to understand patterns of mineral occurrence and coexistence in the context of their environments. Armed with large and growing mineralogical databases, we are now able to address with statistical confidence questions of mineral diversity, disparity, and distributions for different geographical regions, different geological time periods, varying combinations of elements, and for groups of coexisting mineral phases. Work in progress will address the influences of life's origins and evolution, atmospheric and ocean oxygenation, differing tectonic environments, continental growth, biomineralization, and the rise of the terrestrial biosphere on the occurrence and distribution of minerals. Comparisons with other terrestrial planets and moons will clarify the comparative roles of physical, chemical, and biological processes in the evolution of the mineral kingdom.

We conclude that, as in the origins and evolution of life, both chance and necessity play important roles in the origins and evolution of minerals on an Earth-like planet. In many respects, terrestrial planets evolve in deterministic ways, dictated by the abundances of oxygen, silicon, iron, and magnesium. Rocky planets and moons orbiting Sun-like stars will thus inevitably be dominated by the same familiar ferromagnesian oxide and silicate minerals that are abundant in Earth's crust and on the Moon, whose relatively low mineralogical diversity might be close to the minimum that could serve as a baseline for

comparison of Earth-like planets and moons. The significant difference in total mineral diversity between Earth and its Moon and, presumably, between other Earth-like planets and the Moon's baseline mineralogy, points to the likelihood that both chance and necessity play nontrivial roles in the nature and distribution of mineral species—roles that should be amenable to study with our ability to exploit large and growing mineralogical data resources, coupled with statistical analysis.

In conclusion, Earth's near-surface mineralogy is dominated by deterministic factors—principal rock-forming minerals are a necessary consequence of terrestrial worlds. Nevertheless, were Earth's history to be replayed, and thousands of mineral species discovered and characterized anew, it is probable that numerous species would differ from species known today. Thus, we conclude that Earth, the only known living world, is unique in its mineralogical realm as well.

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