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Carbon mineral ecology: Predicting the undiscovered minerals of carbon

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ABSTRACT

Studies in mineral ecology exploit mineralogical databases to document diversity-distribution relationships of minerals—relationships that are integral to characterizing "Earth-like" planets. As carbon is the most crucial element to life on Earth, as well as one of the defining constituents of a planet's near-surface mineralogy, we focus here on the diversity and distribution of carbon-bearing minerals. We applied a Large Number of Rare Events (LNRE) model to the 403 known minerals of carbon, using 82 922 mineral species/locality data tabulated in http://mindat.org (as of 1 January 2015). We find that all carbon-bearing minerals, as well as subsets containing C with O, H, Ca, or Na, conform to LNRE distributions.

Our model predicts that at least 548 C minerals exist on Earth today, indicating that at least 145 carbon-bearing mineral species have yet to be discovered. Furthermore, by analyzing subsets of the most common additional elements in carbon-bearing minerals (i.e., 378 C + O species; 282 C + H species; 133 C + Ca species; and 100 C + Na species), we predict that approximately 129 of these missing carbon minerals contain oxygen, 118 contain hydrogen, 52 contain calcium, and more than 60 contain sodium. The majority of these as yet undescribed minerals are predicted to be hydrous carbonates, many of which may have been overlooked because they are colorless, poorly crystalized, and/or water-soluble.

We tabulate 432 chemical formulas of plausible as yet undiscovered carbon minerals, some of which will be natural examples of known synthetic compounds, including carbides such as calcium carbide (CaC_2), crystalline hydrocarbons such as pyrene ($C_{16}H_{10}$), and numerous oxalates, formates, anhydrous carbonates, and hydrous carbonates. Many other missing carbon minerals will be isomorphs of known carbon minerals, notably of the more than 100 different hydrous carbonate structures. Surveys of mineral localities with the greatest diversity of carbon minerals, coupled with information on varied C mineral occurrences, point to promising locations for the discovery of as yet undescribed minerals.

Keywords: Carbonates, hydrocarbons, oxalates, formates, carbides, mineral ecology, philosophy of mineralogy

INTRODUCTION

A fascinating focus of research in astrobiology and space science is the search for, and characterization of, Earth-like planets. However, a universally accepted definition of "Earth-like" has not been forthcoming. Astronomical factors, most importantly a planetary radius and density similar to Earth's, coupled with a stable orbit within the star's habitable zone (i.e., the torroidal volume in which liquid water is stable), are often cited and discoveries of such extrasolar bodies are justifiably newsworthy, including Kepler 186f (Quintana et al. 2014), Kepler 438b and 442b (Torres et al. 2015), and Kepler 452b (Jenkins et al. 2015). These characteristics, which can be deduced from astronomical observations, are presumably important for the emergence of life. Size, density, and orbital parameters, however, are not by themselves sufficient for life's origins. In particular, geodynamic, geochemical, and mineralogical criteria that promote liquid water and a dynamic carbon cycle must also be present for life as we know it to emerge.

Carbon-bearing minerals, which have diversified significantly over Earth history, are important indicators of a planet's carbon and water cycles, and thus its ability to initiate and sustain life. Given the importance of a few key mineral-forming elements in stars—notably C, O, Si, Mg, and Fe—the parsimonious primordial mineralogy of all stellar nebulae is likely to be similar. Four carbon-bearing nanophases—diamond and graphite (both allotropes of C), cohenite (Fe_3C), and moissanite (SiC)—occur commonly in pre-solar grains (Hazen et al. 2008, 2013a), and are plausible mineralogical starting points for all terrestrial planets. A dozen additional C minerals that appear in chondrite meteorites may also be deterministic features of most planetary systems. However, more varied carbon minerals, including extensive carbonate formations precipitated by microbial communities (Walter et al. 1980; Sumner 1997; Grotzinger and Knoll 1999; Allwood et

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al. 2006; Lepot et al. 2008), and other C-bearing minerals found in Archean rocks older than 2.5 billion years (Hazen 2013), may differentiate Earth from many other astronomically "Earth-like" planets. Subsequent biological processes have led to numerous additional carbonate and organic mineral phases, both through biomineralization (Runnegar 1987; Warthmann et al. 2000; Mann 2001; Dove et al. 2003; Lee et al. 2007; Dove 2010) and as a consequence of atmospheric oxygenation (Hazen et al. 2008; Sverjensky and Lee 2010; Canfield 2014; Lyons et al. 2014). Most of the 403 carbon minerals approved by the International Mineralogical Association (IMA) as of 1 January 2015 (http://rruff.info/ima) are thus biologically mediated. Accordingly, Earth's carbon minerals illustrate principles of mineral evolution and underscore the dynamic co-evolution of the geosphere and biosphere (Hazen et al. 2008, 2012, 2013a, 2013b, 2013c; Golden et al. 2013)—mineralogical aspects that may set Earth apart from most planets of similar mass, density, and orbit.

The principal objective of this contribution is to assess the full diversity of carbon-bearing minerals on Earth—criteria that contribute to understanding the mineralogical basis of "Earth-like." Open-access mineralogical databases, including comprehensive lists of mineral species (rruff.info/ima; Downs 2006) and mineral locality information (notably the crowd-sourced database, http://mindat.org), facilitate studies of the diversity and distribution of carbon minerals (Hazen 2014). In this contribution, we describe statistical analyses of the diversity and distribution of carbon minerals—an approach we call "mineral ecology" (Hazen et al. 2015a, 2015b; Hystad et al. 2015a, 2015b). We demonstrate from frequency distribution relationships that more than 25% of carbon minerals in Earth's crust have yet to be discovered and described, and we propose the identities and possible localities of numerous undescribed carbon minerals.

CARBON MINERAL ACCUMULATION CURVES

Large Number of Rare Events (LNRE) models

Hystad et al. (2015a) reported that the relationship between the diversity and distribution of mineral species is similar to the frequency distribution of words in a book: typically a few words and phrases occur many times, but most words and phrases are used only once or twice. These rare words and phrases can thus be analyzed to identify the idiosyncratic authorship of an unsigned text, and they conform to a Large Number of Rare Events (LNRE) frequency distribution (Baayen 2001; Evert and Baroni 2008).

Mineral ecology exploits mineralogical databases to identify deterministic vs. stochastic aspects of mineral evolution. Of the more than 5000 species approved by the International Mineralogical Association (rruff.info/ima), relatively few minerals dominate Earth's crustal volume and are very common (i.e., approximately 100 species have been reported from more than 1000 localities in mindat.org). However, most mineral species are rare: 22% of species are known from only one locality, and more than half of all minerals are reported from 5 or fewer localities (mindat.org). Thus, mineral occurrences conform to a LNRE distribution (Hazen et al. 2015a).

When applied to mineral statistics, LNRE distributions can be exploited to estimate the numbers and nature of as yet undiscovered species (Hystad et al. 2015a; Hazen et al. 2015b). Here we apply a Generalized Inverse Gauss-Poisson (GIGP) function to the 403 known minerals of carbon, using 82 922 mineral species/locality data tabulated in mindat.org (as of January 2015). We find that carbon-bearing minerals, of which 101 (more than 25%) are known at only one locality, conform to a LNRE distribution (Table 1; Fig. 1a). We also examine subsets of all carbon-bearing minerals that incorporate O, H, Ca, or Na to document further the nature of Earth's "missing" carbon minerals.

Earth's carbon mineral diversity

LNRE models are particularly useful because one can derive the expected rate of discovery of new mineral species as more mineral/locality data are reported (assuming that new data are acquired with the same analytical techniques and protocols as in the past). Thus, for example, data from January 2015 include 403 C mineral species and 82 922 mineral/locality data. If we extrapolate the upper curve in Figure 1b to 160 000 carbon mineral/locality data, then the carbon mineral accumulation curve predicts that an additional ~50 carbon mineral species will have been discovered. Furthermore, continued extrapolation to the right of the accumulation curve in Figure 1b leads to the prediction that at least 548 C minerals occur on Earth today, indicating that at least 145 species have yet to be discovered and described.

This number is a minimum estimate of missing species for two reasons. First, our calculation is based on the assumption that minerals will continue to be discovered by exactly the same procedures that have been used in the past. However, as new techniques and protocols are introduced, the rate of discovery is expected to increase. For example, exploitation of portable

Table 1. Parameters for LNRE distributions of carbon minerals, including those for all C minerals, as well as for C ± O, C ± Ca, C ± H, and C ± Na

Elements	No. of data	No. of minerals	No. predicted	No. of missing	%Missing	LNRE[a]	Maximum *m*	*p*-value
All C	82922	403	548	145	26.5	GIGP	14	0.0004
C + O	79694	378	507	129	25.4	fZM	8	0.0018
C – O	3228[b]	25	41	16	39.0			
C + H	23301	282	400	118	29.5	GIGP, fZM	5	0.74
C – H	59621	121	200	79	39.5	GIGP, fZM	5	0.37
C + Ca	40280	133	185	52	28.1	GIGP, fZM	3	0.11
C – Ca	42642	270	383	113	29.5	GIGP, fZM	6	0.60
C + Na	1406[b]	100	163	63	38.7			
C – Na	81516	303	385	82	21.3	GIGP	7	0.16

Notes: "No. of data" indicates the number of mineral species-locality data recoded in http://mindat.org as of January 2015. Columns headed "No. of minerals," "No. predicted," and "No. missing" indicate numbers of carbon mineral species that are known, predicted to exist on Earth today, and predicted to be undiscovered, respectively. "LNRE" indicates the type of Large Number of Rare Events distribution employed (GIGP = generalized inverse Gauss-Poisson; fZM = finite Zipf-Mandelbrot). "Maximum *m*" is the number of locality bins employed in the LNRE regression analysis. The *p*-value indicates the probability of the LNRE model fitting the data at least this well by chance alone.

[a] Hystad et al. (2015a) document derivations of GIGP- and fZM-type LNRE models.

[b] This sample size is too small to obtain a valid LNRE distribution; No. of minerals is determined by difference.

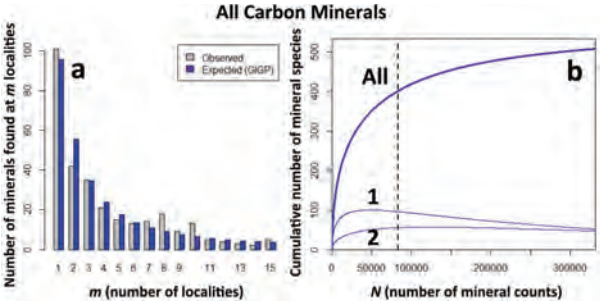

FIGURE 1. (**a**) Frequency spectrum analysis of 403 carbon-bearing minerals, with 82 922 individual mineral-locality data (from http://mindat.org as of January 2015), employed a Generalized Inverse Gauss-Poisson (GIGP) function to model the number of mineral species for minerals found at from one to 14 localities (Hystad et al. 2015a). (**b**) This model facilitates the prediction of the mineral species accumulation curve (upper curve, "All"), which plots the number of expected C mineral species (*y*-axis) as additional mineral species/locality data (*x*-axis) are discovered. The vertical dashed line indicates data recorded as of January 2015 in mindat.org. The model also predicts the varying numbers of mineral species known from exactly one locality (curve 1) or from exactly two localities (curve 2). Note that the number of mineral species from only one locality is now decreasing, whereas the number from two localities is now increasing, though it will eventually decrease. We predict that the number of minerals known from two localities will surpass those from one locality when the number of species-locality data exceeds ~300 000. (Color online.)

Raman spectrometers in the field, widespread use of transmission electron microscopy in nano-mineral characterization, or, perhaps ironically, targeted mineral searches stimulated by predictions such as those in this contribution, will each lead to more rapid identification of new species than the rate of discovery predicted by our model.

A second reason that our prediction of 145 missing carbon minerals represents a minimum estimate is that we have employed locality data from mindat.org without modification. In fact, rare minerals from a single contemporaneous and geographically restricted lithologic unit are sometime recorded as multiple localities on mindat.org. For example, Edward Grew (personal communications) notes that the rare boron mineral homilite ($Ca_2Fe^{2+}B_2Si_2O_{10}$) is recorded from nine localities on mindat.org, but these "localities" represent only two distinct paragenetic events. Mindat.org thus systematically underreports the numbers of the rarest minerals found at exactly one or two localities—a bias that results in lower estimates of missing minerals.

An important related advance, currently under development but as yet incomplete, will be the calculation of errors associated with the extrapolations of numbers of missing minerals. Hints regarding the magnitudes of errors are provided by performing calculations on subsets of the mineral/locality data, as well as by application of alternative LNRE formulations. Thus, Hystad et al. (2015a) found that estimates of missing minerals are reproducible to better than ±3% when random subsets of 50% or 25% of all mineral/locality data are employed. Larger differences to ±10% in predicted numbers of missing minerals are found when different LNRE formulations (i.e., GIGP vs. finite Zipf-Mandelbrot; Hystad et al. 2015a) are applied to the same data sets. Therefore, until more precise error propagation calculations are available, we suggest that ±10% represents a conservative error estimate for all such predictions.

In addition to the accumulation curve for all carbon minerals, Figure 1b also illustrates curves for the expected numbers of carbon minerals known from exactly one or two localities as the total number of species/locality data grows. Note that the number of minerals from only one locality increases rapidly when relatively few mineral/locality data are available, but then levels off and begins to decline—a consequence of better coverage and therefore fewer unique finds. By contrast, the number of C minerals known from exactly two localities will continue to rise at least through the discovery of >200 000 mineral/locality data. Eventually, with >300 000 data the number of C mineral species documented from two localities will surpass those known from only one locality. In this regard, the ratio of minerals known from one vs. two localities is a rough measure of the maturity of Earth's mineral documentation (Hazen et al. 2015b).

Details of Earth's missing carbon minerals can be gleaned from additional LNRE analyses of elements in combination with carbon. Carbon minerals are known to incorporate more than 50 other major chemical elements (Table 2). Of these coexisting elements, the most common are carbon plus oxygen with 378 species, carbon plus hydrogen with 282 species, carbon plus calcium with 133 species, and carbon plus sodium with 100 species. Other common coexisting elements (mostly in carbonate minerals) include the rare earth elements (REE) La through Lu (60 species), Al (59), Mg (58), Si (58), S (41), F (39), Cl (38), Cu (35), U (31), Y (30), Fe (30), Ba (29), and Pb (28). Although it is logical to predict that most missing carbon-bearing species are hydrous carbonates of these elements, LNRE analysis and accumulation curves facilitate more quantitative prediction of the as yet undiscovered carbon minerals. Accordingly, we have analyzed LNRE distributions for minerals in which carbon coexists with O, H, Ca, and Na (Table 1; Figs. 2–5).

Carbon plus oxygen. The frequency distribution of 378 mineral species with coexisting carbon and oxygen, based on 79 694 mineral/locality data (Fig. 2a), closely parallels that of all carbon minerals (Fig. 1a). This similarity is not surprising, given that 94% of carbon-bearing minerals also incorporate oxygen (mostly carbonates, but also oxalates). Our analysis employs a fZM-type LNRE model to predict that a total of 507 oxygen-bearing carbon minerals exist on Earth, suggesting that approximately 129 of these species remain to be discovered (Fig. 2b). Note that this value also suggests that approximately (548 – 507) = 41 carbon minerals without oxygen (presumably mostly carbide and hydrocarbon minerals) occur on Earth. Only 25 carbon-bearing minerals without oxygen are presently known; thus, we estimate that at least 16 such species remain to be discovered and described.

Carbon plus hydrogen. The frequency distribution of 282 mineral species in which carbon and hydrogen coexist is calculated based on 23 301 species/locality data. These data result in LNRE distributions based on both GIGP and finite Zipf-Mandelbrot (fZM) models (Hystad et al. 2015a; Table 1; Fig. 3a). Extrapolation of the accumulation curve (Fig. 3b) leads to prediction of a total of 400 minerals with both carbon and hydrogen on Earth, with 118 hydrous carbon mineral species remaining to be discovered.

A complementary calculation can be performed for the 121 carbon minerals that do not incorporate hydrogen, based on 59 621 mineral/locality data. This number is misleading, however, because almost 90% of these data relate to the nine commonest anhydrous carbonates: calcite ($CaCO_3$; with 24 394 reported localities), dolomite [$CaMg(CO_3)_2$; 7250 localities], siderite ($FeCO_3$; 5738 localities), cerussite ($PbCO_3$; 4658 localities), aragonite ($CaCO_3$; 2895 localities), ankerite [$FeMg(CO_3)_2$; 2798 localities], smithsonite ($ZnCO_3$; 2219 localities), rhodochrosite ($MnCO_3$; 1663 localities), and magnesite ($MgCO_3$; 1182 localities). Therefore, fewer than 7000 species/locality data document the rare anhydrous C species that are necessary to define the LNRE distribution. The resulting LNRE fit is less well constrained than the LNRE model for carbon minerals containing oxygen (Table 1; Fig. 3a). We predict a total of 200 anhydrous carbon minerals exist on Earth, with approximately 79 yet to be discovered and described (Fig. 3d). Note that the sums of predicted missing C plus H minerals (~118 species) and C minus H minerals (~79 species) is 197, which is significantly greater than the prediction of 145 missing species based on all carbon minerals (Fig. 1b). We conclude that the numbers of predicted missing minerals based on combinations of elements are less well constrained than for all C minerals; we suggest that errors of ±20% may apply to all such predictions by extrapolation.

Carbon plus calcium. Approximately one-third of carbon minerals (133 of 403 species) also incorporate calcium. Both GIGP- and fZM-type LNRE models based on 40 280 mineral/locality data predict a total of approximately 185 C plus Ca species, pointing to the existence of at least 52 species that have not yet been discovered and described (Figs. 4a and 4b). A similar evaluation of the 270 carbon-bearing minerals lacking Ca, based on 42 642 data, predicts a total of approximately 383 species, of which 113 are undescribed (Figs. 4c and 4d). The number of predicted missing minerals with C and Ca (52), plus those for C without Ca (113), totals ~165 species—a number 14% greater than the estimate of 145 species derived from analysis of all carbon minerals.

Carbon plus sodium. In spite of the existence of 100 mineral species in which carbon coexists with sodium, the 1406 mineral species/locality data that document these generally rare phases are too few for a reliable LNRE analysis. However, we have employed a GIGP-type LNRE model to analyze the remaining 303 mineral species (81 516 data) for carbon minerals *without* sodium (Figs. 5a and 5b). Our accumulation curve analysis predicts that 385 C minerals without Na exist, which implies that at least 82

TABLE 2. Coexisting essential elements in carbon minerals

Element	No. of C minerals	Element	No. of C minerals
O	379	La	12
H	283	Nd	10
Ca	134	Zr	9
Na	100	Ti	6
REE (La-Lu)	60	Cr	6
Al	59	Hg	5
Mg	58	Co	4
Si	58	Nb	4
S	41	Li	3
F	39	As	3
Ce	38	Te	3
Cu	34	Bi	3
U	31	V	2
Cl	30	Ta	2
Fe	30	W	2
Y	30	Th	2
Ba	29	Be	1
Pb	28	Ge	1
P	21	Br	1
Mn	21	Mo	1
Sr	21	Cd	1
K	18	I	1
Ni	16	Gd	1
N	13	Er	1
Zn	13	Yb	1
B	12		

Notes: Numbers for 51 elements are based on mineral species and chemical formulas in http://rruff.info/ima as of 1 January 2015. No known carbon-bearing minerals incorporate 19 mineral-forming elements: Sc, Ga, Se, Rb, Ru, Rh, Pd, Ag, In, Sn, Sb, Cs, Hf, Re, Os, Ir, Pt, Au, or Tl.

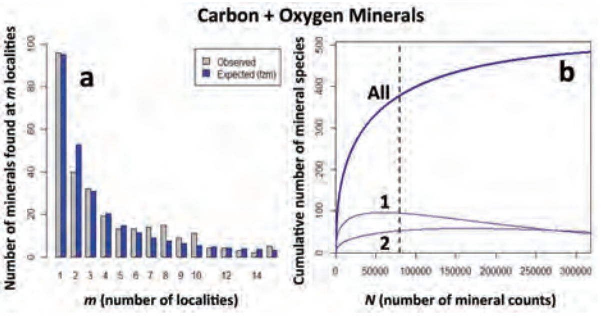

FIGURE 2. (**a**) Frequency spectrum analysis of 378 minerals containing C + O, with 79 694 individual mineral-locality data (from http://mindat.org as of January 2015), employed a finite Zipf-Mandelbrot (fZM) function to model the number of mineral species for minerals found at from 1 to 8 localities (Hystad et al. 2015a). (**b**) The mineral species accumulation curve predicts that at least 507 C + O minerals exist on Earth, suggesting that approximately 129 species have yet to be described. (Color online.)

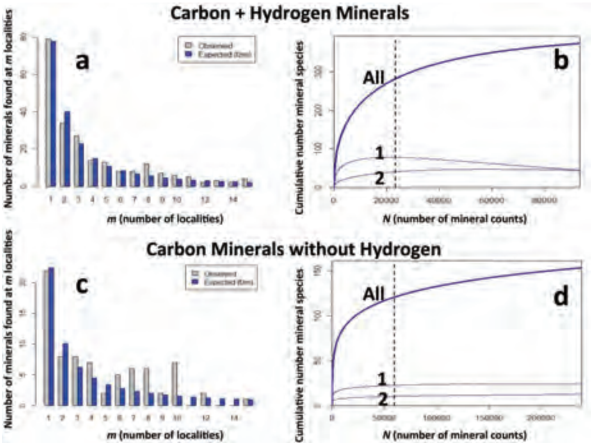

FIGURE 3. (**a** and **c**) Frequency spectrum analyses of 282 minerals containing C + H, with 23 301 individual mineral-locality data, and 121 minerals containing C but not H, with 59 621 data (from http://mindat.org as of January 2015), employed finite Zipf-Mandelbrot models (Hystad et al. 2015a). (**b** and **d**) Mineral species accumulation curves predict that approximately 400 C minerals with H and 200 C minerals without H exist on Earth. (Color online.)

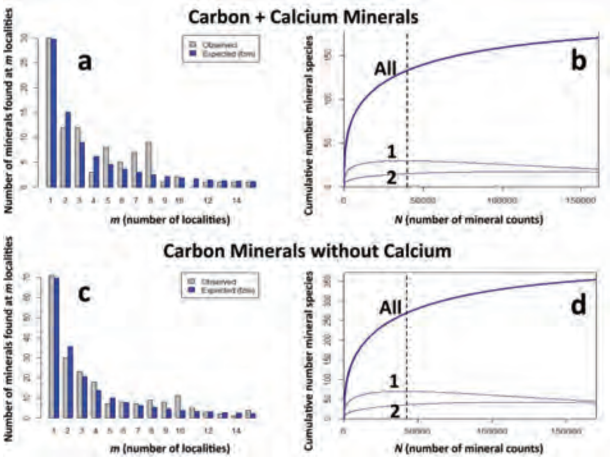

FIGURE 4. (**a** and **c**) Frequency spectrum analyses of 133 minerals containing C + Ca, with 40 280 individual mineral-locality data, and 383 minerals containing C but not O, with 42 642 data (from http://mindat.org as of January 2015), employed finite Zipf-Mandelbrot models (Hystad et al. 2015a). (**b** and **d**) Mineral species accumulation curves predict that ~185 C minerals with Ca and 270 C minerals without Ca exist on Earth (Color online.).

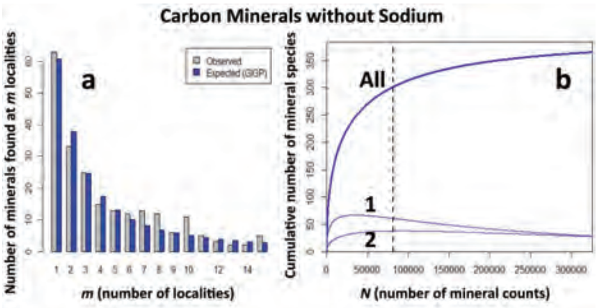

FIGURE 5. (**a**) Frequency spectrum analysis of 303 minerals containing carbon without sodium, with 81 516 individual mineral-locality data (from http://mindat.org as of January 2015), employed a Generalized Inverse Gauss-Poisson (GIGP) function to model the number of mineral species for minerals found at from one to seven localities (Hystad et al. 2015a). (**b**) The mineral species accumulation curve predicts that at least 385 C minerals without Na exist on Earth, and by difference, there must be approximately 163 minerals with C + Na to reach our predicted total of 548 C-bearing minerals. (Color online.)

as yet undiscovered mineral species incorporate C without Na. Furthermore, if 145 carbon minerals are missing, we conclude that at least 63 of the missing C minerals contain sodium; thus ~39% of carbon minerals containing Na have yet to be discovered (Table 1). This percentage is significantly higher than for all C minerals (26.5%), as well as for minerals of carbon plus oxygen (25.4%), carbon plus hydrogen (29.5%), and carbon plus calcium (29.5%)—results that echo the findings of Hazen et al. (2015b), who suggest that sodium minerals are relatively underreported because they are typically colorless and poorly crystallized, and thus difficult to identify in hand specimen. Furthermore, sodium minerals are often water-soluble and thus may be ephemeral.

THE UNDISCOVERED MINERALS OF CARBON

The preceding analysis points to the existence of numerous as yet undescribed carbon mineral species on Earth, many of which are compounds of O, H, Ca, and Na. Having recognized this gap in our mineralogical knowledge, we adopt two strategies to predict plausible identities and possible localities for some of these missing carbon minerals.

The first strategy relies on the similarity of many natural minerals to synthetic compounds; therefore, some of the as yet undescribed carbon minerals will match known synthetic chemicals. We conducted a survey of 10 260 inorganic carbon-bearing compounds with two, three, four, or five different chemical elements tabulated in the International Crystal Structure Database as of 27 July 2015 (ICSD; http://icsd.fiz-karlsruhe.de), as well as inorganic compounds listed in the *Handbook of Chemistry and Physics* (http://hbcpnetbase.com). From these data we selected 242 examples of synthetic mineral-like compounds with no known mineral equivalents, but with chemical formulas that are similar to those of known minerals (Table 3a). Note that expansion of our search to the 3784 ICSD compounds with six to ten different elements would have significantly increased the number of plausible minerals owing to the combinatorial richness of carbon chemistry.

The second strategy involves identifying plausible carbon minerals that are isomorphs of known minerals. In Table 3b we identify 190 additional selected examples not recorded in Table 3a, based primarily on the substitution of common crustal elements. We rely primarily on well-known crystal chemical principles: Isomorphism commonly results from substitution of cations of identical charge and similar ionic radius. Note, however, that the following analysis, as well as the tabulations on which they are based, only consider chemical formulas. We do not differentiate among the multiple polymorphs of many carbon-bearing minerals [e.g., SiC, $CaCO_3$, $Na_2Ca(CO_3)_2$, and $Mg_5(CO_3)_4(OH)_2{\cdot}5H_2O$], which would further enrich the list of plausible undiscovered minerals.

Carbide minerals

Carbide minerals, which generally require extremely reducing conditions, are rare at or near Earth's surface. Nevertheless, 10 carbide minerals (phases with Si, Fe, Ni, Co, Cr, Ti, V, Nb, Ta, and W) have been described and approved by the International Mineralogical Association's Commission on New Minerals, Nomenclature and Classification, mostly in extraterrestrial samples (Hazen et al. 2013a). Our analysis is consistent with the existence of additional as yet undescribed carbides on Earth (Tables 3a and 3b).

ICSD catalogs more than 100 synthetic carbides with C plus one additional element, some of which are also known as minerals. These diverse synthetic phases point to possible as yet undiscovered minerals, 27 of which are listed in Table 3a, with two additional plausible natural carbides recorded in Table 3b. Notably absent from the list of reported natural carbides is calcium carbide, a commercial chemical that is used in the production of acetylene, as fuel for miners' lamps, and as an explosive in novelty toy cannons. Calcium carbide is produced commercially in electric arc furnaces by the reaction of lime and coke (Morehead and Chalmot 1896), with acetylene generated

TABLE 3a. Selected possible formulas of missing carbon minerals based on known mineral-like synthetic compounds with two, three, four, or five different elements

Formula of synthetic compound	Type formula [Known minerals]
Carbides	
VC	$XC\ [X = Si, Ti, Nb, Ta, W]$
NiC	
ZrC	
MoC	
MgC_2	XC_2
CaC_2	
SrC_2	
Be_2C	X_2C
V_2C	
Co_2C	
Nb_2C	
Mo_2C	
Ta_2C	
W_2C	
Li_2C_2	X_2C_2
Na_2C_2	
K_2C_2	
Cr_3C	$X_3C\ [X = Fe]$
Mn_3C	
Co_3C	
Ni_3C	
Al_4C_3	X_4C_3
V_4C_3	
Cr_7C_3	X_7C_3
Mn_7C_3	
Fe_7C_3	
$Mn_{23}C_6$	$X_{23}C_6\ [X = Fe, Cr]$
Oxalates	
$Li_2(C_2O_4)$	$A_2^{1+}(C_2O_4)\ [A = Na]$
$K_2(C_2O_4)$	
$Rb_2(C_2O_4)$,	
$Cs_2(C_2O_4)$	
$Ag_2(C_2O_4)$	
$CsH(C_2O_4)$	$A^{1+}H(C_2O_4)$
$(NH_4)H(C_2O_4)$	
$K_2(C_2O_4)\cdot H_2O$	$A_2^{1+}(C_2O_4)\cdot H_2O\ [A = (NH_4)]$
$Rb_2(C_2O_4)\cdot H_2O$	
$Cs_2(C_2O_4)\cdot H_2O$	
$LiH(C_2O_4)\cdot H_2O$	$A^{1+}H(C_2O_4)\cdot H_2O$
$NaH(C_2O_4)\cdot H_2O$	
$KH_3(C_2O_4)_2\cdot 2H_2O$	$A^{1+}H_3(C_2O_4)_2\cdot 2H_2O$
$K_2Cu(C_2O_4)_2\cdot 4H_2O$	$A_2^{1+}B^{2+}(C_2O_4)_2\cdot 4H_2O$
$K_2Co(C_2O_4)_2\cdot 6H_2O$	$A_2^{1+}B^{2+}(C_2O_4)_2\cdot 6H_2O$
$K_2Ni(C_2O_4)_2\cdot 6H_2O$	
$Rb_2(UO_2)_2(C_2O_4)_3$	$A_2^{1+}B_2^{2+}(C_2O_4)_3$
$Na_2Mg_2(C_2O_4)_3\cdot 2H_2O$	$A_2^{1+}B_2^{2+}(C_2O_4)_3\cdot 2H_2O$
$Na_2Co_2(C_2O_4)_3\cdot 2H_2O$	
$K_6(UO_2)_2(C_2O_4)_5\cdot 10H_2O$	$A_6^{1+}B_2^{2+}(C_2O_4)_5\cdot 10H_2O$
$LiB(C_2O_4)_2$	$A^{1+}B^{3+}(C_2O_4)_2$
$NaB(C_2O_4)_2$	
$KB(C_2O_4)_2$	
$LiB(C_2O_4)_2\cdot H_2O$	$A^{1+}B^{3+}(C_2O_4)_2\cdot H_2O$
$Na_3Cr(C_2O_4)_3\cdot 5H_2O$	$A_3^{1+}B^{3+}(C_2O_4)_3\cdot 5H_2O$
$K_3Fe(C_2O_4)_3$	$A_3^{1+}B^{3+}(C_2O_4)_3$
$KCr(C_2O_4)_2\cdot 2H_2O$	$A^{1+}B^{3+}(C_2O_4)_2\cdot 2H_2O$
$NaY(C_2O_4)_2\cdot 4H_2O$	$A^{1+}B^{3+}(C_2O_4)_2\cdot 4H_2O$
$K_3Co(C_2O_4)_3\cdot 2H_2O$	$A_3^{1+}B^{3+}(C_2O_4)_3\cdot 2H_2O$
$K_3Al(C_2O_4)_3\cdot 3H_2O$	$A_3^{1+}B^{3+}(C_2O_4)_3\cdot 3H_2O\ [AB = KFe]$
$K_3Mn(C_2O_4)_3\cdot 3H_2O$	
$K_3Cr(C_2O_4)_3\cdot 3H_2O$	
$Na_3Al(C_2O_4)_3\cdot 5H_2O$	$A_3^{1+}B^{3+}(C_2O_4)_3\cdot 5H_2O$
$Na_3Cr(C_2O_4)_3\cdot 5H_2O$	
$Na_3Fe(C_2O_4)_3\cdot 5H_2O$	
$Na_4La_2(C_2O_4)_5\cdot 2H_2O$	$A_4^{1+}B_2^{3+}(C_2O_4)_5\cdot 2H_2O$
$Na_4Ce_2(C_2O_4)_5\cdot 2H_2O$	
$Na_2Cr(C_2O_4)_2(OH)\cdot 3H_2O$	$A_2^{1+}B^{3+}(C_2O_4)_2(OH)\cdot 3H_2O$
$Na_4Zr(C_2O_4)_4\cdot 3H_2O$	$A_4^{1+}B^{4+}(C_2O_4)_4\cdot 3H_2O$
$K_4Th(C_2O_4)_4\cdot 4H_2O$	$A_4^{1+}B^{4+}(C_2O_4)_4\cdot 4H_2O$
$Ba(C_2O_4)\cdot H_2O$	$A^{2+}(C_2O_4)\cdot H_2O\ [A = Ca]$
$Co(C_2O_4)\cdot 2H_2O$	$A^{2+}(C_2O_4)\cdot 2H_2O\ [A = Mg, Ca, Mn, Fe]$
$Ni(C_2O_4)\cdot 2H_2O$	
$Zn(C_2O_4)\cdot 2H_2O$	
$Pb(C_2O_4)\cdot 2H_2O$	
$Cu(C_2O_4)\cdot 3H_2O$	$A^{2+}(C_2O_4)\cdot 3H_2O\ [A = Ca, Mn]$
$Cd(C_2O_4)\cdot 3H_2O$	
$(UO_2)(C_2O_4)\cdot 3H_2O$	
$Mn_2(C_2O_4)(OH)_2$	$A_2^{2+}(C_2O_4)(OH)_2$
$Cd_2(C_2O_4)(OH)_2$	
$(UO_2)\ _2(C_2O_4)(OH)_2\cdot 2H_2O$	$A_2^{2+}(C_2O_4)(OH)_2\cdot 2H_2O$
$Sr_2H_2(C_2O_4)_3$	$A_2^{2+}H_2(C_2O_4)_3$
$Sr_2H_2(C_2O_4)_3\cdot 2H_2O$	$A_2^{2+}H_2(C_2O_4)_3\cdot 2H_2O$
$Fe_4(C_2O_4)(PO_4)_2\cdot 2H_2O$	$A_4^{2+}(C_2O_4)(PO_4)_2\cdot 2H_2O$
$Zn_4(C_2O_4)(PO_4)_2\cdot 2H_2O$	
$BaCu(C_2O_4)_2\cdot 6H_2O$	$A^{2+}B^{2+}(C_2O_4)_2\cdot 6H_2O$
$Ca_2Zr(C_2O_4)_4\cdot 5H_2O$	$A_2^{2+}B^{4+}(C_2O_4)_4\cdot 5H_2O$
$Pb_2(C_2O_4)Cl_2$	$A_2^{2+}(C_2O_4)X_2^{1-}$
$Bi(C_2O_4)(OH)$	$A^{3+}(C_2O_4)(OH)$
$V^{3+}O(C_2O_4)\cdot 5H_2O$	$A^{3+}O(C_2O_4)\cdot 5H_2O$
$Bi_2(C_2O_4)_3\cdot 6H_2O$	$A_2^{3+}(C_2O_4)_3\cdot 6H_2O$
$La_2(C_2O_4)(OH)_4\cdot 6H_2O$	$A_2^{3+}(C_2O_4)(OH)_4\cdot 6H_2O$
$Bi_2(C_2O_4)_3\cdot 8H_2O$	$A_2^{3+}(C_2O_4)_3\cdot 8H_2O$
$La_2(C_2O_4)_3\cdot 10H_2O$	$A_2^{3+}(C_2O_4)_3\cdot 10H_2O\ [A = Ce]$
$Th(C_2O_4)_2\cdot 2H_2O$	$A^{4+}(C_2O_4)_2\cdot 2H_2O$
$U(C_2O_4)_2\cdot 2H_2$	
$U(C_2O_4)_2\cdot 6H_2O$	$A^{4+}(C_2O_4)_2\cdot 6H_2O$
$Ti_2O_3(C_2O_4)\cdot 2H_2O$	$A_2^{4+}O_3(C_2O_4)\cdot 2H_2O$
$Ti_2O_3(C_2O_4)\cdot 3H_2O$	$A_2^{4+}O_3(C_2O_4)\cdot 3H_2O$
$U_2(C_2O_4)F_6\cdot 2H_2O$	$A_2^{4+}(C_2O_4)F_6\cdot 2H_2O$
$(UO_2)(C_2O_4)\cdot 3H_2O$	$(A^{6+}O_2)(C_2O_4)\cdot 3H_2O$
$(UO_2)_2(C_2O_4)(OH)_2\cdot 2H_2O$	$(A^{6+}O_2)_2(C_2O_4)(OH)_2\cdot 2H_2O$
Formates	
$Na(HCOO)$	$A^{1+}(HCOO)$
$K(HCOO)$	
$Rb(HCOO)$	
$(NH_4)(COOH)$	
$KH(HCOO)_2$	$A^{1+}H(HCOO)_2$
$RbH(HCOO)_2$	
$CsH(HCOO)_2$	
$Li(HCOO)\cdot H_2O$	$A^{1+}(HCOO)\cdot H_2O$
$Na(HCOO)\cdot 2H_2O$	$A^{1+}(HCOO)\cdot 2H_2O$
$LiNa(HCOO)_2\cdot H_2O$	$A^{1+}B^{1+}(HCOO)_2\cdot H_2O$
$Mg(HCOO)_2$	$A^{2+}(HCOO)_2\ [A = Ca]$
$Mn(HCOO)_2$	
$Cu(HCOO)_2$	
$Zn(HCOO)_2$	
$Sr(HCOO)_2$	
$Cd(HCOO)_2$	
$Pb(HCOO)_2$	
$BaH(HCOO)_3$	$A^{2+}H(HCOO)_3$
$Mn(HCOO)_2\cdot 2H_2O$	$A^{2+}(HCOO)_2\cdot 2H_2O\ [A = Mg]$
$Fe(HCOO)_2\cdot 2H_2O$	
$Ni(HCOO)_2\cdot 2H_2O$	
$Cu(HCOO)_2\cdot 2H_2O$	
$Zn(HCOO)_2\cdot 2H_2O$	
$Sr(HCOO)_2\cdot 2H_2O$	
$Cd(HCOO)_2\cdot 2H_2O$	
$Cu(HCOO)_2\cdot 4H_2O$	$A^{2+}(HCOO)_2\cdot 4H_2O$
$(UO_2)(HCOO)_2\cdot H_2O$	$A^{2+}(HCOO)_2\cdot H_2O$
$Co(HCOO)(OH)$	$A^{2+}(HCOO)(OH)$
$Cu(HCOO)(OH)$	
$Pb_2O(HCOO)_2$	$A_2^{2+}O(HCOO)_2$
$Cr_3(HCOO)_6\cdot 2H_2O$	$A_3^{2+}(HCOO)_6\cdot 2H_2O$
$Sc(HCOO)_3$	$A^{3+}(HCOO)_3$
$Y(HCOO)_3$	
$Bi(HCOO)_3$	
$Y(HCOO)_3\cdot 2H_2O$	$A^{3+}(HCOO)_3\cdot 2H_2O$
$Fe_3^{3+}O(HCOO)_7\cdot 4H_2O$	$A_3^{3+}O(HCOO)_7\cdot 4H_2O$
$V^{4+}O(HCOO)_2\cdot H_2O$	$A^{4+}O(HCOO)\cdot H_2O$
Other mineral-like organic crystals	
*Mg, Fe, Co metalloporphyrins	various synthetic and natural porphyrins
*$C_{16}H_{10}$	pyrene
*$C_{18}H_{12}$	chrysene
*$C_{18}H_{12}$	tetracene
Anhydrous carbonates	
$K_2(CO_3)$	$A_2^{1+}(CO_3)\ [A = Li, Na]$
$Rb_2(CO_3)$	
$Cs_2(CO_3)$	
$Ag_2(CO_3)$	
$Tl_2(CO_3)$	

(Continued on next page)

TABLE 3a.—*CONTINUED*

Formula of synthetic compound	Type formula [Known minerals]
*$(NH_4)_2(CO_3)$	
$LiNa(CO_3)$	$A^{1+}B^{1+}(CO_3)$
$LiK(CO_3)$	
$KAg(CO_3)$	
$Na_5CoO_2(CO_3)$	$A_5^{1+}B^{1+}O_2(CO_3)$
$Na_5NiO_2(CO_3)$	
$Na_5CuO_2(CO_3)$	
$K_5CuO_2(CO_3)$	
$K_2Mg(CO_3)_2$	$A_2^{1+}B^{2+}(CO_3)_2$ [*AB* = NaMg, NaCa, KCa, NaCu]
$K_2Cu(CO_3)_2$	[3 polymorphs occur for $Na_2Ca(CO_3)_2$]
$Tl_2Cu(CO_3)_2$	
$Rb_2Sr_2(CO_3)_3$	$A_2^{1+}B_2^{2+}(CO_3)_3$ [*AB* = NaCa]
$Cs_2Sr_2(CO_3)_3$	
$Cs_2Ba_2(CO_3)_3$	
$K_6Be_4O(CO_3)_6$	$A_6^{1+}B_4^{2+}O(CO_3)_6$
$NaLa(CO_3)_2$	$A^{1+}B^{3+}(CO_3)_2$
$Na_5Y(CO_3)_4$	$A_5^{1+}B^{3+}(CO_3)_4$
$KLaO(CO_3)$	$A^{1+}B^{3+}O(CO_3)$
$Cs_4(UO_2)(CO_3)_3$	$A_4^{1+}(UO_2)(CO_3)_3$ [*A* = Na, K]
$Tl_4(UO_2)(CO_3)_3$	
$(NH_4)_4(UO_2)(CO_3)_3$	
$Cu(CO_3)$	$A^{2+}(CO_3)$ [*A* = Ca, Mg, Mn, Fe, etc.]
$MgCd(CO_3)_2$	$A^{2+}B^{2+}(CO_3)_2$ [*AB* = CaMg, CaFe, etc.]
$Sr_2CuO_2(CO_3)$	$A_2^{2+}B^{2+}O_2(CO_3)$
$Sr_5Mn^{3+}{}_4O_{10}(CO_3)$	$A_5^{2+}B_4^{3+}O_{10}(CO_3)$
$Sr_4Fe_2O_6(CO_3)$	$A_4^{2+}B_2^{3+}O_6(CO_3)$
$Sr_4Co_2O_6(CO_3)$	
$Ba_3Y_2O_5(CO_3)$	$A_3^{2+}B_2^{3+}O_5(CO_3)$
$Sr_4Fe_2O_6(CO_3)$	$A_4^{2+}B_2^{4+}O_6(CO_3)$
$Sr_4Sc_2O_6(CO_3)$	
*$Al_2(CO_3)_3$	$A_2^{3+}(CO_3)_3$
*$La_2(CO_3)_3$	
$La_2O_2(CO_3)$	$A_2^{3+}O_2(CO_3)$ [*A* = Bi]
Hydrous carbonates	
$Na_2(CO_3)\cdot 1.5H_2O$	$A_2^{1+}(CO_3)\cdot 1.5H_2O$
$K_2(CO_3)\cdot 1.5H_2O$	
$Rb_2(CO_3)\cdot 1.5H_2O$	
$Cs_2(CO_3)\cdot 3H_2O$	$A_2^{1+}(CO_3)\cdot 3H_2O$
$Na_2(CO_3)\cdot 7H_2O$	$A_2^{1+}(CO_3)\cdot 7H_2O$
$CsH(CO_3)$	$A^{1+}H(CO_3)$ [*A* = Na]
$Rb_4H_2(CO_3)_3\cdot H_2O$	$A_4^{1+}H_2(CO_3)_3\cdot H_2O$
$NaK(CO_3)\cdot 6H_2O$	$A^{1+}B^{1+}(CO_3)\cdot 6H_2O$
$NaK_2H(CO_3)_2\cdot 2H_2O$	$A^{1+}B_2^{1+}H(CO_3)_2\cdot 2H_2O$
$NaRb_2H(CO_3)_2\cdot 2H_2O$	
$NaCo_4(CO_3)_3(OH)_3\cdot 3H_2O$	$A^{1+}B_4^{2+}(CO_3)_3(OH)_3\cdot 3H_2O$
$Rb_2Cu(CO_3)_2\cdot H_2O$	$A_2^{1+}B^{2+}(CO_3)_2\cdot H_2O$
$Na_2Co(CO_3)_2\cdot 4H_2O$	$A_2^{1+}B^{2+}(CO_3)_2\cdot 4H_2O$ [*AB* = KMg]
$K_2Co(CO_3)_2\cdot 4H_2O$	
$K_2Ni(CO_3)_2\cdot 4H_2O$	
$Rb_2Co(CO_3)_2\cdot 4H_2O$	
$Rb_2Ni(CO_3)_2\cdot 4H_2O$	
$Na_2Zn_3(CO_3)_4\cdot 3H_2O$	$A_2^{1+}B_3^{2+}(CO_3)_4\cdot 3H_2O$
$KMgH(CO_3)_2\cdot 4H_2O$	$A^{1+}B^{2+}H(CO_3)_2\cdot 4H_2O$
$KNiH(CO_3)_2\cdot 4H_2O$	
$K_6Be_4O(CO_3)_6\cdot 7H_2O$	$A_6^{1+}B_4^{2+}O(CO_3)_6\cdot 7H_2O$
$Na_2Zn_3(CO_3)_4\cdot 3H_2O$	$A_2^{1+}B_3^{2+}(CO_3)_4\cdot 3H_2O$
$NaPb_2(CO_3)_2(OH)$	$A^{1+}B_2^{2+}(CO_3)_2(OH)$
$Na_2Y(CO_3)_2(OH)$	$A_2^{1+}B^{3+}(CO_3)_2(OH)$
$KAl(CO_3)(OH)_2\cdot H_2O$	$A^{1+}B^{3+}(CO_3)(OH)_2\cdot H_2O$
$Na_6Th(CO_3)_5\cdot 12H_2O$	$A_6^{1+}B^{4+}(CO_3)_5\cdot 12H_2O$
$Na_6Ce(CO_3)_5\cdot 12H_2O$	
*$Be(CO_3)\cdot xH_2O$	$A^{2+}(CO_3)\cdot xH_2O$
$Co_2(CO_3)(OH)_2$	$A_2^{2+}(CO_3)(OH)_2$ [*A* = Mg, Fe, Ni, Cu, Zn]
$Pb_2O(CO_3)\cdot 2H_2O$	$A_2^{2+}O(CO_3)\cdot 2H_2O$
$MgCr(CO_3)_2\cdot 3H_2O$	$A^{2+}B^{2+}(CO_3)_2\cdot 3H_2O$
$BaCa(CO_3)_2\cdot 3H_2O$	
$Sr_2(UO_2)(CO_3)_3\cdot 8H_2O$	$A_2^{2+}B^{2+}(CO_3)_3\cdot 8H_2O$
$Ca_4Al_2(CO_3)(OH)_{12}\cdot 5H_2O$	$A_4^{2+}B_2^{3+}(CO_3)(OH)_{12}\cdot 5H_2O$
$Ni_2Al(CO_3)(OH)_6$	$A_2^{2+}B^{3+}(CO_3)(OH)_6$
$Y(CO_3)(OH)$	$A^{3+}(CO_3)(OH)$
$La_2(CO_3)_2(OH)_2$	$A_2^{3+}(CO_3)_2(OH)_2$
$Nd_2(CO_3)_2(OH)_2$	
Carbonates with halogens	
$K_3(CO_3)F$	$A_3^{1+}(CO_3)X^{1-}$
$Rb_3(CO_3)F$	
$K_2H(CO_3)F\cdot H_2O$	$A_2^{1+}H(CO_3)X^{1-}\cdot H_2O$
$KRb_2(CO_3)F$	$A^{1+}B_2^{1+}(CO_3)X^{1-}$
$RbK_2(CO_3)F$	
$KCa(CO_3)F$	
$KSr(CO_3)F$	$A^{1+}B^{2+}(CO_3)X^{1-}$
$RbCa(CO_3)F$	
$RbSr(CO_3)F$	
$Na_3Co(CO_3)_2Cl$	$A_3^{1+}B^{2+}(CO_3)_2X^{1-}$ [*ABX* = NaMgCl]
$Cs_3Ba_4(CO_3)_3F_5$	$A_3^{1+}B_4^{2+}(CO_3)_3X_5^{1-}$
$KPb_2(CO_3)_2F$	$A^{1+}B_2^{2+}(CO_3)_2X^{1-}$
$Na_2Y(CO_3)F_3$	$A_2^{1+}B^{3+}(CO_3)X_3^{1-}$
$NaLa_2(CO_3)_3F$	$A^{1+}B_2^{3+}(CO_3)_3X^{1-}$
$Na_3Y(CO_3)_2F_2$	$A_3^{1+}B^{3+}(CO_3)_2X_2^{1-}$
$Pb_2(CO_3)Br_2$	$A_2^{2+}(CO_3)X_2^{1-}$ [*AX* = CaF, PbCl]
$Ba_3(CO_3)Cl_4$	$A_3^{2+}(CO_3)X_4^{1-}$
$BaMn(CO_3)F_2$	$A^{2+}B^{2+}(CO_3)X_2^{1-}$
$BaCu(CO_3)F_2$	
$BaZn(CO_3)F_2$	
$BaPb_2(CO_3)_2F_2$	$A^{2+}B_2^{2+}(CO_3)_2X_2^{1-}$
$Ba_2Y(CO_3)_2F_3$	$A_2^{2+}B^{3+}(CO_3)_2X_3^{1-}$
$Ba_3La_2(CO_3)_5F_2$	$A_3^{2+}B_2^{3+}(CO_3)_5X_2^{1-}$
$La(CO_3)F$	$A^{3+}(CO_3)X^{1-}$
Carbonates with other anionic groups	
$Pb_{12}(OH)_{12}(CO_3)(ClO_4)_{10}\cdot 6H_2O$	$A_{12}^{2+}(OH)_{12}(CO_3)(ClO_4)_{10}\cdot 6H_2O$
$Y_2(CO_3)_2(C_2O_4)\cdot 2H_2O$	$A_2^{3+}(CO_3)_2(C_2O_4)\cdot 2H_2O$

Notes: Most of these compounds are tabulated in the International Crystal Structure Database (icsd.fiz-karlsruhe.de). Additional poorly crystallized synthetic phases recorded in the *Handbook of Chemistry and Physics* (hbcpnetbase.com) or chemical supply catalogs are noted with an asterisk (*). We list only those formulas that are similar compositionally to minerals but are not known as minerals. Some compositions have multiple possible structure types.

subsequently by reaction of CaC_2 with water. "Carbide lamps" of miners exploit this instability to produce a steady portable supply of flammable acetylene for illumination. We suggest that lightning strikes near the contact of limestone and coal or other concentrated organic matter might produce small, if ephemeral, quantities of CaC_2.

Additional natural carbide phases that are analogs of synthetic compounds, might include VC, V_4C_3, Cr_3C, Cr_7C_3, Mn_3C, Mn_7C_3, $Mn_{23}C_6$, Fe_7C_3, Co_2C, Co_3C, NiC, Ni_3C, ZrC, MoC, Mo_2C, Mo_3C_2, and W_2C. Less likely because of the extreme reducing conditions and implausible chemical environments required are natural occurrences of the well-known synthetic compounds Be_2C, MgC_2, and Al_4C_3. Nevertheless, unusual circumstances might result in the occurrence of these phases.

As with the 10 approved carbide minerals, new carbide minerals are likely to be found in extremely reducing cosmochemical or geochemical environments, including enstatite chondrite meteorites (Larimer and Bartholomay 1979; Brearley and Jones 1998) and thermally altered carbon-rich deposits such as the contact metamorphism of coal (Melson and Switzer 1966; Larsen and Pedersen 2009).

Organic molecular minerals

Hydrocarbon minerals. Ten hydrocarbon minerals have been recognized as valid species by the IMA. Given the combinatorially vast number of possible hydrocarbon molecules, it is likely that many other such phases await discovery. Of special interest are four natural crystalline polycyclic aromatic hydrocarbon (PAH) minerals: carpathite ($C_{24}H_{12}$; the organic molecule known as coronene), idrialite ($C_{22}H_{14}$; pentacene), kratochvilite ($C_{13}H_{10}$; fluorine), and ravatite ($C_{14}H_{10}$; anthracene). These PAH minerals condense from sooty fires, with melting points of 116

Table 3b. Selected possible missing carbon minerals not listed in Table 3a, based on likely isomorphous substitutions of common elements into known minerals

Predicted isomorphous mineral	Known mineral species
Carbides	
$Cr_4Mn_4NiC_4$	yarlongite [$Cr_4Fe_4NiC_4$]
$Ni_{23}C_6$	haxonite [$(Fe,Ni)_{23}C_6$]
Oxalates	
$Na_2(C_2O_4)\cdot H_2O$	oxammite [$(NH_4)_2(C_2O_4)\cdot H_2O$]
$Na_2Fe(C_2O_4)_2\cdot 2H_2O$	wheatleyite [$Na_2Cu(C_2O_4)_2\cdot 2H_2O$]
$Na_2Mg(C_2O_4)_2\cdot 2H_2O$	
$KNa_3Fe_2(C_2O_4)_4$	antipinite [$KNa_3Cu_2(C_2O_4)_4$]
$KNa_3Mn_2(C_2O_4)_4$	
$K_3Cr^{3+}(C_2O_4)_3\cdot 3H_2O$	minguzzite [$K_3Fe^{3+}(C_2O_4)_3\cdot 3H_2O$]
$NaFeAl(C_2O_4)_3\cdot 8H_2O$	zhemchuzhnikovite [$NaMgAl(C_2O_4)_3\cdot 8H_2O$]
$KMgAl(C_2O_4)_3\cdot 8H_2O$	
$Fe^{2+}(C_2O_4)\cdot H_2O$	whewellite [$Ca(C_2O_4)\cdot H_2O$]
$Sr(C_2O_4)\cdot H_2O$	
$Cu^{2+}(C_2O_4)\cdot 2H_2O$	humboldtine [$Fe^{2+}(C_2O_4)\cdot 2H_2O$]
$Fe^{2+}(C_2O_4)\cdot 3H_2O$	caoxite [$Ca(C_2O_4)\cdot 3H_2O$]
$Sr(C_2O_4)\cdot 3H_2O$	
$Mg_2(C_2O_4)Cl_2\cdot 2H_2O$	novgorodovaite [$Ca_2(C_2O_4)Cl_2\cdot 2H_2O$]
$Y_2(SO_4)_2(C_2O_4)\cdot 8H_2O$	coskrenite-(Ce) [$Ce_2(SO_4)_2(C_2O_4)\cdot 8H_2O$]
$La_2(SO_4)_2(C_2O_4)\cdot 8H_2O$	
$Y_2(C_2O_4)_3\cdot 10H_2O$	deveroite-(Ce) [$Ce_2(C_2O_4)_3\cdot 10H_2O$]
$La_2(C_2O_4)_3\cdot 10H_2O$	
$LaAl(SO_4)_2(C_2O_4)\cdot 12H_2O$	levinsonite-(Y) [$YAl(SO_4)_2(C_2O_4)\cdot 12H_2O$]
Other organic minerals	
$Fe(HCOO)_2$	formicaite [$Ca(HCOO)_2$]
$Fe^{2+}(CH_3COO)_2\cdot H_2O$	hoganite [$Cu^{2+}(CH_3COO)_2\cdot H_2O$]
$Fe(CH_3COO)Cl\cdot 5H_2O$	calclacite [$Ca(CH_3COO)Cl\cdot 5H_2O$]
$Fe(CH_3SO_3)_2\cdot 12H_2O$	ernstburkeite [$Mg(CH_3SO_3)_2\cdot 12H_2O$]
$Ni(CH_3SO_3)_2\cdot 12H_2O$	
$Na_2Mg(SCN)_4\cdot 8H_2O$	julienite [$Na_2Co(SCN)_4\cdot 8H_2O$]
$Na_2Fe(SCN)_4\cdot 8H_2O$	
Anhydrous carbonates	
$Na_2Mn(CO_3)_2$	nyerereite and zemkorite [$Na_2Ca(CO_3)_2$]
$Na_2Ni(CO_3)_2$	
$K_2Mn(CO_3)_2$	
$Na_2Mg_2(CO_3)_3$	shortite [$Na_2Ca_2(CO_3)_3$]
$Na_2Fe^{2+}_2(CO_3)_3$	
$Na_4Y_2(CO_3)_5$	petersenite-(Ce) [$Na_4Ce_2(CO_3)_5$]
$Na_4La_2(CO_3)_5$	
$K_4Ce_2(CO_3)_5$	
$K_4TiZr_2O_4(CO_3)_4$	sabinaite [$Na_4TiZr_2O_4(CO_3)_4$]
$K_2CaPb_3(CO_3)_5$	sanrománite [$Na_2CaPb_3(CO_3)_5$]
$Na_2MgPb_3(CO_3)_5$	
$CaNi(CO_3)_2$	dolomite [$CaMg(CO_3)_2$]
$CaCo(CO_3)_2$	
$SrMg(CO_3)_2$	
$SrMg_3(CO_3)_4$	huntite [$CaMg_3(CO_3)_4$]
$CaFe_3(CO_3)_4$	
$Sr_2O(CO_3)$	shannonite [$Pb_2O(CO_3)$]
$Ba_2O(CO_3)$	
$Ba_6Ca_6Fe(CO_3)_{13}$	benstonite [$Ba_6Ca_6Mg(CO_3)_{13}$]
$Ba_6Mn_6Mg(CO_3)_{13}$	
$FeBi_2O_2(CO_3)_2$	beyerite [$CaBi_2O_2(CO_3)_2$]
$SrBi_2O_2(CO_3)_2$	
$MgY_2(CO_3)_4$	sahamalite-(Ce) [$MgCe_2(CO_3)_4$]
$MgLa_2(CO_3)_4$	
$FeCe_2(CO_3)_4$	
$FeTe^{4+}O_2(CO_3)$	mroseite [$CaTe^{4+}O_2(CO_3)$]
$SrTe^{4+}O_2(CO_3)$	
Hydrous carbonates	
$K_5H_3(CO_3)_4$	wegscheiderite [$Na_5H_3(CO_3)_4$]
$K_2(CO_3)\cdot H_2O$	thermonatrite [$Na_2(CO_3)\cdot H_2O$]
$K_2(CO_3)\cdot 10H_2O$	natron [$Na_2(CO_3)\cdot 10H_2O$]
$Na_2Mg(CO_3)_2\cdot 2H_2O$	pirssonite [$Na_2Ca(CO_3)_2\cdot 2H_2O$]
$Na_2Fe^{2+}(CO_3)_2\cdot 3H_2O$	chalconatronite [$Na_2Cu^{2+}(CO_3)_2\cdot 3H_2O$]
$K_2Fe^{2+}(CO_3)_2\cdot 4H_2O$	baylissite [$K_2Mg(CO_3)_2\cdot 4H_2O$]
$Na_2Fe^{2+}(CO_3)_2\cdot 5H_2O$	gaylussite [$Na_2Ca(CO_3)_2\cdot 5H_2O$]
$K_2Ca(CO_3)_2\cdot 5H_2O$	
$KBe(CO_3)(OH)\cdot 2H_2O$	niveolanite [$NaBe(CO_3)(OH)\cdot 2H_2O$]
$NaMg_4(CO_3)_3(OH)_3\cdot 3H_2O$	kambaldaite [$NaNi_4(CO_3)_3(OH)_3\cdot 3H_2O$]
$NaFe^{2+}{}_4(CO_3)_3(OH)_3\cdot 3H_2O$	
$KNi_4(CO_3)_3(OH)_3\cdot 3H_2O$	
$NaFe^{3+}(CO_3)(OH)_2$	dawsonite [$NaAl(CO_3)(OH)_2$]
$Mg(CO_3)\cdot H_2O$	monohydrocalcite [$Ca(CO_3)\cdot H_2O$]
$Fe(CO_3)\cdot H_2O$	
$Ca(CO_3)\cdot 3H_2O$	nesquehonite [$Mg(CO_3)\cdot 3H_2O$]
$Fe(CO_3)\cdot 3H_2O$	
$Ca(CO_3)\cdot 5H_2O$	lansfordite [$Mg(CO_3)\cdot 5H_2O$]
$Fe(CO_3)\cdot 5H_2O$	
$Mn(CO_3)\cdot 6H_2O$	ikaite [$Ca(CO_3)\cdot 6H_2O$]
$Fe(CO_3)\cdot 6H_2O$	
$Mg_3(CO_3)(OH)_4$	brianyoungite [$Zn_3(CO_3)(OH)_4$]
$Mg_5(CO_3)_2(OH)_6$	hydrozincite [$Zn_5(CO_3)_2(OH)_6$]
$Mg_7(CO_3)_2(OH)_{10}$	sclarite [$Zn_7(CO_3)_2(OH)_{10}$]
$Ca_3(CO_3)_2(OH)_2$	hydrocerussite [$Pb_3(CO_3)_2(OH)_2$]
$Sr_3(CO_3)_2(OH)_2$	
$Ca_2(CO_3)(OH)_2\cdot H_2O$	otwayite [$Ni_2(CO_3)(OH)_2\cdot H_2O$]
$Fe_2(CO_3)(OH)_2\cdot H_2O$	
$Ca_2(CO_3)(OH)_2\cdot 3H_2O$	artinite [$Mg_2(CO_3)(OH)_2\cdot 3H_2O$]
$Fe_2(CO_3)(OH)_2\cdot 3H_2O$	
$Fe_3(CO_3)(OH)_4\cdot 4H_2O$	claraite [$Cu^{2+}{}_3(CO_3)(OH)_4\cdot 4H_2O$]
$Mg_3(CO_3)(OH)_4\cdot 4H_2O$	
$Fe_5(CO_3)_4(OH)_2\cdot 4H_2O$	hydromagnesite [$Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$]
$Fe_5(CO_3)_4(OH)_2\cdot 5H_2O$	dypingite, giorgiosite [$Mg_5(CO_3)_4(OH)_2\cdot 5H_2O$]
$Ca_5(CO_3)_3O(OH)_2$	plumbonacrite [$Pb_5(CO_3)_3O(OH)_2$]
$Sr_5(CO_3)_3O(OH)_2$	
$CuMn(CO_3)(OH)_2$	malachite [$Cu_2(CO_3)(OH)_2$]
$CuFe(CO_3)(OH)_2$	
$Fe_2Mg_2(CO_3)(OH)_6\cdot 2H_2O$	callaghanite [$Cu_2Mg_2(CO_3)(OH)_6\cdot 2H_2O$]
$Cu_2Fe_2(CO_3)(OH)_6\cdot 2H_2O$	
$CaLa(CO_3)_2(OH,H_2O)_2$	ancylite-(La) [$SrLa(CO_3)_2(OH,H_2O)_2$]
$CaCe(CO_3)_2(OH,H_2O)_2$	
$CaCr_2(CO_3)_2(OH)_4\cdot H_2O$	dundasite [$PbAl_2(CO_3)_2(OH)_4\cdot H_2O$]
$BaCr_2(CO_3)_2(OH)_4\cdot H_2O$	
$Fe_4Cr_2(CO_3)(OH)_{12}\cdot 3H_2O$	caresite [$Fe^{2+}{}_4Al_2(CO_3)(OH)_{12}\cdot 3H_2O$]
$Ca_4Fe_2(CO_3)(OH)_{12}\cdot 3H_2O$	
$Ca_6Cr_2CO_3(OH)_{16}\cdot 4(H_2O)$	hydrotalcite [$Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$]
$MgAl_2(CO_3)_2(OH)_4\cdot 3H_2O$	alumohydrocalcite [$CaAl_2(CO_3)_2(OH)_4\cdot 3H_2O$]
$CaFe_2(CO_3)_2(OH)_4\cdot 3H_2O$	
$Fe_4Al_2(CO_3)(OH)_{12}\cdot 2H_2O$	carbonate-cyanotrichite [$Cu^{2+}_4Al_2(CO_3)(OH)_{12}\cdot 2H_2O$]
$Cu_4Fe_2(CO_3)(OH)_{12}\cdot 2H_2O$	
$Cr_5(CO_3)(OH)_{13}\cdot 5H_2O$	scarbroite [$Al_5(CO_3)(OH)_{13}\cdot 5H_2O$]
$Fe^{3+}{}_5(CO_3)(OH)_{13}\cdot 5H_2O$	
Hydrous uranium carbonates with [$(UO_2)(CO_3)_3$] groups	
$Na_2Mg(UO_2)(CO_3)_3\cdot 6H_2O$	andersonite [$Na_2Ca(UO_2)(CO_3)_3\cdot 6H_2O$]
$K_2Mg_3[(UO_2)(CO_3)_3]_2\cdot 7H_2O$	línekite [$K_2Ca_3[(UO_2)(CO_3)_3]_2\cdot 7H_2O$]
$Fe_2(UO_2)(CO_3)_3\cdot 18H_2O$	bayleyite [$Mg_2(UO_2)(CO_3)_3\cdot 18H_2O$]
$Mg_2(UO_2)(CO_3)_3\cdot 11H_2O$	liebigite [$Ca_2(UO_2)(CO_3)_3\cdot 11H_2O$]
$Fe_2(UO_2)(CO_3)_3\cdot 11H_2O$	
$FeMg(UO_2)(CO_3)_3\cdot 12H_2O$	swartzite [$CaMg(UO_2)(CO_3)_3\cdot 12H_2O$]
$CaFe(UO_2)(CO_3)_3\cdot 12H_2O$	
$Ca_3Fe^{2+}_3[(UO_2)(CO_3)_3]_2(OH)_4\cdot 18H_2O$	rabbittite [$Ca_3Mg^{2+}_3[(UO_2)(CO_3)_3]_2(OH)_4\cdot 18H_2O$]
$CaY(UO_2)_{24}(CO_3)_8Si_4O_{28}\cdot 60H_2O$	lepersonnite-(Gd) [$CaGd(UO_2)_{24}(CO_3)_8Si_4O_{28}\cdot 60H_2O$]
$CaLa(UO_2)_{24}(CO_3)_8Si_4O_{28}\cdot 60H_2O$	
Hydrous yttrium/Rare earth element carbonates	
$NaLa(CO_3)_3\cdot 6H_2O$	adamsite-(Y) [$NaY(CO_3)_3\cdot 6H_2O$]
$NaCe(CO_3)_3\cdot 6H_2O$	
$Na_3La(CO_3)_3\cdot 3H_2O$	shomiokite-(Y) [$Na_3Y(CO_3)_3\cdot 3H_2O$]
$Na_3Ce(CO_3)_3\cdot 3H_2O$	
$Na_3La(CO_3)_3\cdot 6H_2O$	lecoqite-(Y) [$Na_3Y(CO_3)_3\cdot 6H_2O$]
$Na_3Ce(CO_3)_3\cdot 6H_2O$	
$CaY_2(CO_3)_4\cdot H_2O$	galgenbergite-(Ce) [$CaCe_2(CO_3)_4\cdot H_2O$]
$CaLa_2(CO_3)_4\cdot H_2O$	
$CaLa_2(CO_3)_4\cdot 6H_2O$	kimuraite-(Y) [$CaY_2(CO_3)_4\cdot 6H_2O$]
$CaCe_2(CO_3)_4\cdot 6H_2O$	
$Ca_2La_2(CO_3)_4(OH)_2\cdot 3H_2O$	kamphaugite-(Y) [$Ca_2Y_2(CO_3)_4(OH)_2\cdot 3H_2O$]
$Ca_2Ce_2(CO_3)_4(OH)_2\cdot 3H_2O$	
$Ca_2La_2(SiO_3)_4(CO_3)\cdot H_2O$	kainosite-(Y) [$Ca_2Y_2(SiO_3)_4(CO_3)\cdot H_2O$]
$Ca_2Ce_2(SiO_3)_4(CO_3)\cdot H_2O$	
$Y_2(CO_3)_3\cdot 4H_2O$	calkinsite-(Ce) [$Ce_2(CO_3)_3\cdot 4H_2O$]
$La_2(CO_3)_3\cdot 4H_2O$	
$Y_2(CO_3)_3\cdot 8H_2O$	lanthanite-(La) [$La_2(CO_3)_3\cdot 8H_2O$]
Hydrous uranium/REE carbonates	
$Cu_2La_2(UO_2)(CO_3)_5(OH)_2\cdot 1.5H_2O$	astrocyanite-(Ce) [$Cu_2Ce_2(UO_2)(CO_3)_5(OH)_2\cdot 1.5H_2O$]
$La_8(UO_2)_{16}O_8(CO_3)_{16}(OH)_8\cdot 39H_2O$	bijvoetite-(Y) [$Y_8(UO_2)_{16}O_8(CO_3)_{16}(OH)_8\cdot 39H_2O$]

(Continued on next page)

TABLE 3b.—*CONTINUED*

Predicted isomorphous mineral	Known mineral species
$La_2O_4(UO_2)_4(CO_3)_3 \cdot 14H_2O$	kamotoite-(Y) [$Y_2O_4(UO_2)_4(CO_3)_3 \cdot 14H_2O$]
$CaLa_2(UO_2)(CO_3)_4(OH)_2 \cdot 6H_2O$	shabaite-(Nd) [$CaNd_2(UO_2)(CO_3)_4(OH)_2 \cdot 6H_2O$]
$NaBa_3(Ca,U)La(CO_3)_6 \cdot 3H_2O$	mckelveyite-(Y) [$NaBa_3(Ca,U)Y(CO_3)_6 \cdot 3H_2O$]
Carbonates with halogens	
$Na_7Fe(CO_3)_2(HCO_3)_2F_4$	barentsite [$Na_7Al(CO_3)_2(HCO_3)_2F_4$]
$K_7Al(CO_3)_2(HCO_3)_2F_4$	
$NaLa(CO_3)F_2$	horváthite-(Y) [$NaY(CO_3)F_2$]
$NaCe(CO_3)F_2$	
$Na_3Y_2(CO_3)_4F$	lukechangite-(Ce) [$Na_3Ce_2(CO_3)_4F$]
$Na_3La_2(CO_3)_4F$	
$Na_3MgMn^{2+}(CO_3)_3F$	rouvilleite [$Na_3CaMn^{2+}(CO_3)_3F$]
$Na_3FeMn^{2+}(CO_3)_3F$	
$NaMn_3(CO_3)_2F_3 \cdot H_2O$	sheldrickite [$NaCa_3(CO_3)_2F_3 \cdot H_2O$]
$KCa_3(CO_3)_2F_3 \cdot H_2O$	
$Ca_2Sr(CO_3)_2F_2$	podlesnoite [$Ca_2Ba(CO_3)_2F_2$]
$Ca_4Fe(UO_2)_2(CO_3)_6F_2 \cdot 17H_2O$	albrechtschraufite [$Ca_4Mg(UO_2)_2(CO_3)_6F_2 \cdot 17H_2O$]
$Sr_2La(CO_3)_3F$	kukharenkoite-(La) [$Ba_2La(CO_3)_3F$]
$Ba_2Y(CO_3)_3F$	
$Sr_2Y(CO_3)_3F$	
$BaY(CO_3)_2F$	huanghoite-(Ce), qaqarssukite-(Ce) [$BaCe(CO_3)_2F$]
$BaLa(CO_3)_2F$	
$PbCe(CO_3)_2F$	
$FeBiO(CO_3)F$	kettnerite [$CaBiO(CO_3)F$]
$SrBiO(CO_3)F$	
$CaY_2(CO_3)_3F_2$	parisite-(Ce) [$CaCe_2(CO_3)_3F_2$]
$CaLa_2(CO_3)_3F_2$	
$Ca_2Y_3(CO_3)_5F_3$	röntgenite-(Ce) [$Ca_2Ce_3(CO_3)_5F_3$]
$Ca_2La_3(CO_3)_5F_3$	
$CaLa(CO_3)_2F$	synchysite-(Y) [$CaY(CO_3)_2F$]
$Sr_3Ce_2(CO_3)_5F_2$	cebaite-(Ce) [$Ba_3Ce_2(CO_3)_5F_2$]
$MgTh(CO_3)_2F_2 \cdot 3H_2O$	thorbastnäsite [$CaTh(CO_3)_2F_2 \cdot 3H_2O$]
$CaU(CO_3)_2F_2 \cdot 3H_2O$	
Carbonates with other anionic groups	
$Na_3Ca(PO_4)(CO_3)$	bradleyite [$Na_3Mg(PO_4)(CO_3)$]
$Na_6Ni_2(CO_3)_4(SO_4)$	tychite [$Na_6Mg_2(CO_3)_4(SO_4)$]
$K_6Mg_2(CO_3)_4(SO_4)$	
$K_4(SO_4)(CO_3)$	burkeite [$Na_4(SO_4)(CO_3)$]
$K_8(UO_2)(CO_3)_3(SO_4)_2 \cdot 3H_2O$	ježekite [$Na_8(UO_2)(CO_3)_3(SO_4)_2 \cdot 3H_2O$]
$Mg_2(SO_4)(CO_3) \cdot 4H_2O$	rapidcreekite [$Ca_2(SO_4)(CO_3) \cdot 4H_2O$]
$Fe_2(SO_4)(CO_3) \cdot 4H_2O$	
$Sr_3Mn^{4+}(SO_4)(CO_3)(OH)_6 \cdot 12H_2O$	jouravskite [$Ca_3Mn^{4+}(SO_4)(CO_3)(OH)_6 \cdot 12H_2O$]
$Fe_2Pb^{2+}_5(SO_4)_3(CO_3)(OH)_6$	caledonite [$Cu_2Pb^{2+}_5(SO_4)_3(CO_3)(OH)_6$]
$Sr_2(S_2O_3)(CO_3)$	fassinaite [$Pb_2(S_2O_3)(CO_3)$]
$Ba_2(S_2O_3)(CO_3)$	
$Mn_3Si(OH)_6(SO_4)(CO_3) \cdot 12H_2O$	thaumasite [$Ca_3Si(OH)_6(SO_4)(CO_3) \cdot 12H_2O$]
$Sr_4Al^{3+}_2Si_4O_{10}(SO_4)(CO_3)_2(OH)_4$	kegelite [$Pb_4Al_2Si_4O_{10}(SO_4)(CO_3)_2(OH)_4$]
$Mn_7(SiO_4)_3(CO_3)$	galuskinite [$Ca_7(SiO_4)_3(CO_3)$]
$La_2(SiO_4)(CO_3)$	iimoriite-(Y) [$Y_2(SiO_4)(CO_3)$]
$Ce_2(SiO_4)(CO_3)$	
$KH_4(CO_3)(BO_3) \cdot 2H_2O$	qilianshanite [$NaH_4(CO_3)(BO_3) \cdot 2H_2O$]
$Fe_2(HBO_3)(CO_3) \cdot 5H_2O$	canavesite [$Mg_2(HBO_3)(CO_3) \cdot 5H_2O$]
$Ca_4FeB_4O_6(CO_3)_2(OH)_6$	borcarite [$Ca_4MgB_4O_6(CO_3)_2(OH)_6$]
$Ca_4Fe^{3+}_3(BO_3)_3(CO_3)O_3$	gaudefroyite [$Ca_4Mn^{3+}_3(BO_3)_3(CO_3)O_3$]
$Ca_{12}Fe_4Al(SiO_4)_4(BO_3)_3(CO_3)_5 \cdot H_2O$	harkerite [$Ca_{12}Mg_4Al(SiO_4)_4(BO_3)_3(CO_3)_5 \cdot H_2O$]
$Ca_2Fe_9(AsO_4)_4(CO_3)(OH)_8 \cdot 11H_2O$	tyrolite [$Ca_2Cu^{2+}_9(AsO_4)_4(CO_3)(OH)_8 \cdot 11H_2O$]

to 438 °C (Fig. 6). We predict that at least three other common PAH phases (Table 3a; Fig. 6) likely occur as natural crystals: pyrene ($C_{16}H_{10}$), and chrysene and tetracene (both isomers of $C_{18}H_{12}$), with melting points from 145 to 357 °C. As with other PAH minerals, these as yet undiscovered phases may occur near coal mine fires or in other thermally altered coal deposits.

Oxalates. Twenty-one oxalate minerals have been documented, along with hundreds of varied synthetic oxalates recorded in the International Crystal Structure Database. These known compositions suggest numerous plausible mineral analogs and isomorphs. Table 3a tabulates 72 mineral-like synthetic oxalates recorded in ICSD that have not been documented as mineral species (an additional 19 postulated isomorphs of oxalate minerals appear in Table 3b). Of the synthetic phases, the most common elements are K (in 15 compounds), Na (13), and Cr (5), whereas Li, Co, REE, and U each are represented by four synthetic oxalates. Mineral-like synthetic oxalates with single cations include $A^{1+}_2(C_2O_4)$ with A^{1+} = Li, K, Rb, Cs, and Ag [also represented by the mineral natroxalate, $Na_2(C_2O_4)$]; $A^{1+}_2(C_2O_4) \cdot H_2O$ with A^{1+} = K, Rb, and Cs; $A^{2+}(C_2O_4) \cdot 2H_2O$ with A^{2+} = Co, Ni, Zn, and Pb [also humboldtine group minerals with A^{2+} = Mg (glushinskite), Mn (lindbergite), and Fe (humboldtine), as well as weddellite [$Ca(C_2O_4) \cdot 2H_2O$)]; and $A^{2+}(C_2O_4) \cdot 3H_2O$ with A^{2+} = Cu, Cd, and (UO_2) [also minerals with A^{2+} = Ca (caoxite) and Mn (falottaite)]. Synthetic double cation oxalates include $A^{1+}B^{3+}(C_2O_4)_2$ with $A^{1+}B^{3+}$ = LiB, NaB, and KB; $A^{1+}_3B^{3+}(C_2O_4)_3 \cdot 3H_2O$ with $A^{1+}B^{3+}$ = KAl, KMn, and KCr [as well as the mineral minguzzite, $K_3Fe^{3+}(C_2O_4)_3 \cdot 3H_2O$]; and $A^{1+}_3B^{3+}(C_2O_4)_3 \cdot 5H_2O$, with $A^{1+}B^{3+}$ = NaAl, NaCr, and NaFe. Given the similarities of many of these synthetic phases to known minerals, it is likely that many oxalates await discovery.

Natural oxalates (Table 3b) also point to as yet undiscovered minerals. One significant subset has the formula $A^{2+}(C_2O_4) \cdot nH_2O$. Substitution of alternate divalent cations, including (in order of increasing ionic radius) Ni, Mg, Cu, Zn, Co, Fe, Mn, Cd, Ca, Sr, Pb, and Ba, point to numerous possible as yet undescribed isomorphous minerals. A similar diversity exists for oxalates with +1 cations, including antipinite [$KNa_3Cu_2(C_2O_4)_4$], minguzzite [$K_3Fe^{3+}(C_2O_4)_3 \cdot 3H_2O$], and oxammite [$(NH_4)_2(C_2O_4) \cdot H_2O$]. Isomorphs with alternate +1 (Na, K, Rb, Ag, Hg, NH_4), +2 (see above), and +3 (Al, Fe, Cr, Ti, Mn, Co) cations possess a potential combinatorial richness that hints at numerous as yet undescribed oxalate minerals (Table 3b).

A survey of the occurrence of natural oxalates suggests possible search strategies for new minerals. Oxalates are often found as taphonomic minerals associated with the alteration of biological materials, including cacti (weddelite), guano (oxammite), lichen (glushinskite), leaf litter (hoganite, paceite), and fossil egg shells of birds (oxammite), as well as in coal (humboldtine, stepanovite, whewellite). Oxalate minerals with transition metal elements have been discovered in locations where plant material interacts with ore bodies, such as tree roots penetrating copper deposits (moolooite, wheatleyite). Thus, a systematic search for new oxalate minerals might involve more focused attention to microscopic crystals associated with live or decaying organisms.

Other organic minerals. More than two dozen additional minerals that incorporate organic molecules are known. Of special note are minerals containing formate $(HCOO)^-$ groups, including formicaite [$Ca(HCOO)_2$] and dashkovaite [$Mg(HCOO)_2 \cdot 2H_2O$]. ICSD lists more than 100 metallo-formate compounds, many of which are mineral-like. Table 3a lists 37 potential formate minerals with +1, +2, or +3 cations. We do not tabulate the numerous synthetic formates with combinations of 2 or more cations that are recorded by ICSD and that could occur as natural formate-bearing crystals.

Other minerals that contain acetate $(CH_3COO)^-$ groups, including hoganite [$Cu(CH_3COO)_2 \cdot H_2O$], calclacite [$Ca(CH_3COO)Cl \cdot 5H_2O$], and paceite [$CaCu(CH_3COO)_2 \cdot 6H_2O$], coupled with such diverse phases as ernstburkeite [$Mg(CH_3SO_3)_2 \cdot 12H_2O$] and julienite [$Na_2Co(SCN)_4 \cdot 8H_2O$], underscore the potential diversity of organic minerals. Numerous other related minerals are

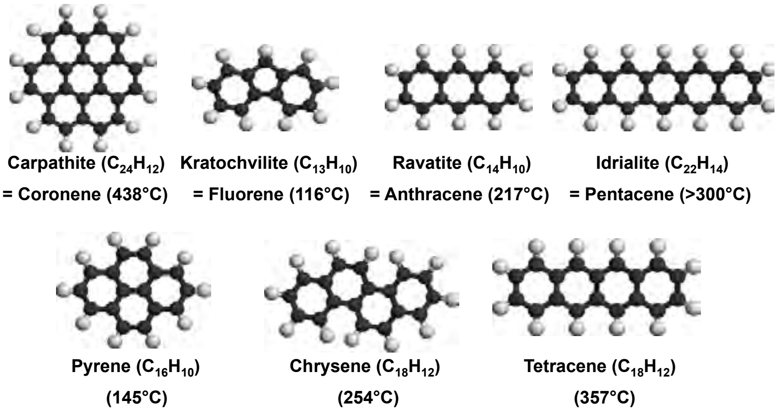

FIGURE 6. Known (top row) and predicted (bottom row) polycyclic aromatic hydrocarbon (PAH) minerals, with melting points. Coronene, fluorene, anthracene, and pentacene are known minerals with melting points from 116 to 438 °C. Pyrene, tetracene, and chrysene are common PAHs not yet identified in natural crystals with similar melting, from points from 145 to 357 °C.

plausible, for example by substitution of other divalent cations (Table 3b). Many such phases may have been overlooked as a consequence of their relative rarity, inconspicuous nature, and biological setting.

Of special interest is the Ni-porphyrin mineral abelsonite ($NiC_{31}H_{32}N_4$), which is found on fracture surfaces of oil shale (Milton et al. 1978). Numerous biological porphyrins, including heme (the Fe-bearing pigment in red blood cells) and chlorophyll (a group of related Mg-porphyrin molecules important to photosynthesis), are known (e.g., Kadish et al. 2010). However, none of these biophorphyin molecules have been found in natural crystals, leaving abelsonite as the only known mineral incorporating a porphyrin molecule. Interestingly, Ni-porphyrins are not widely used in natural biological systems; therefore, abelsonite may represent the accumulation of bioporphyrins like chlorophyll that have undergone cation exchange (Mason et al. 1989). The prospect of discovering additional examples of mineral porphyins with different divalent cations thus seems likely.

Anhydrous carbonates

Anhydrous carbonates include some of the most volumetrically abundant minerals in Earth's near-surface environment. Nevertheless, carbonates without H constitute only 106 of the 403 documented carbon-bearing mineral species. Hints to possible as yet undocumented examples are found in both catalogs of synthetic compounds (Table 3a) and known minerals (Table 3b).

Synthetic anhydrous carbonates. Table 3a lists 38 mineral-like anhydrous carbonates that have not yet been identified in nature—data that suggest numerous examples may await discovery. The most frequent elements in these phases are K (in 8 compounds), Sr (8), Na (6), Cu (6), La (4), and Cs (4). Anhydrous alkali carbonates are particularly well represented in Table 3a, comprising 20 of the 38 entries. Of note is formula type $A_2^{1+}(CO_3)$, known only as synthetic compounds for A^{1+} = K, Rb, Cs, Ag, Tl, and NH_4, but as the minerals zabuyelite [$Li_2(CO_3)$], and gregoryite and natrite [both $Na_2(CO_3)$]. Note, for example, that anhydrous ammonium carbonate, $(NH_4)_2CO_3$, though readily available as a chemical reagent, has not yet been described in nature. This phase might be found naturally in association with teschemacherite [$(NH_4)HCO_3$], which is found in guano (along with a dozen other C-bearing minerals) and is the only known natural ammonium carbonate. In addition, single anhydrous carbonates of Cu^{2+}, Al, and La, though known as synthetic phases, have not been described as minerals, nor have several synthetic oxy-carbonates, including $KLaO(CO_3)$, $Sr_2CuO_2(CO_3)$, and $La_2O_2(CO_3)$. These formula types are not yet recorded as minerals. Note that "$Be(CO_3)$" is commonly available as a chemical reagent; however, no crystal structure has been reported and it appears that this compound is always hydrated (Everest 1973; see below).

Also of note are numerous synthetic double-carbonate phases, for example $A^{1+}B^{1+}(CO_3)$ with $A^{1+}B^{1+}$ = LiNa, LiK, and KAg; $A_5^{1+}B^{1+}O_2(CO_3)$ with $A^{1+}B^{1+}$ = NaCo, NaNi, NaCu, and KCu (note the unusual 1+ oxidation states of Co, Ni, and Cu); and $A_2^{1+}B_2^{2+}(CO_3)_3$ with $A^{1+}B^{2+}$ = RbSr, CsSr, and CsBa [as well as the mineral shortite, $Na_2Ca_2(CO_3)_3$]. The $A_2^{1+}B^{2+}(CO_3)_2$ formula type is of special interest, as it is represented by several minerals with AB = NaMg, NaCa, KCa, and NaCu, including 2 different structure types for $Na_2Ca(CO_3)_3$ (nyerereite and zemkorite), but also by synthetic compounds with $A^{1+}B^{2+}$ = KMg, KCu, and TlCu, which might also occur naturally.

A survey of known mineral formula types (Table 3b) adds 27 plausible anhydrous carbonate minerals not listed in Table 3a, and points to numerous other potential isomorphous anhydrous carbonate minerals that are related to known minerals by cation substitution, as amplified in the following sections.

Calcite and aragonite groups. Numerous phases with the general formula $A^{2+}(CO_3)$ are known as minerals, most of which occur in the rhombohedral calcite (A^{2+} = Mg, Ca, Mn, Fe, Co, Ni, Zn, Cd) or orthorhombic aragonite (A^{2+} = Ca, Sr, Ba, Pb) structures. These important species include the most common and volumetrically dominant carbon-bearing compounds in Earth's crust (Reeder 1983; Speer 1983). The only anhydrous carbonate of a common divalent element that is known as a synthetic compound, but has not yet been recorded as a mineral, is $Cu(CO_3)$.

Dolomite group. Minerals of the dolomite group conform to the general formula $A^{2+}B^{2+}(CO_3)_2$, where the divalent A and B cations are ordered in the rhombohedral structure. Known species include *AB* = CaFe (ankerite), CaMg (dolomite), CaMn (kutnohorite), CaZn (minrecordite), and BaMg (norsethite). One key to stability of the ordered dolomite structure (as opposed to the disordered arrangement of divalent cations in the calcite structure) is sufficient size differential between the two cations. All known dolomite group minerals have a cation radius difference ~0.17 Å—the minimum observed for Mn (crystal radius 0.97 Å) vs. Ca (1.14 Å) in kutnohorite. However, this difference is not, by itself, sufficient to form the ordered structure (Reeder 1983). Additional as yet undescribed dolomite group carbonates might include those with Ca-Ni, Ca-Cu, Ca-Co, and CaCd (the latter known as a synthetic phase). Note that, although Sr and Ba typically enter the orthorhombic aragonite structure rather than the rhombohedral dolomite structure, the observation of dolomite-type norsethite [$BaMg(CO_3)_2$], raises the possibility of additional dolomite group phases, for example with SrMg, SrFe, and BaFe.

Nyerereite and zemkorite type binary carbonates. Several binary carbonates incorporate +1 and +2 cations. Most notable in this group are those with general formula $A_2^{1+}B^{2+}(CO_3)_2$. Known minerals include $A^{1+}B^{2+}$ = NaMg (eitelite), NaCa (nyerereite and zemkorite), NaCu (juangodoyite), and KCa (bütschliite and fairchildite). These phases point to the existence of many other plausible minerals with A^{1+} = Na, K, or (NH_4) and B^{2+} = Mg, Mn, Fe, Co, Ni, Cu, Zn, Sr, Cd, Ba, or Pb.

Burbankite group. The burbankite group of triple carbonates includes minerals with the general formula $(A^{1+}B^{2+}C^{3+})_6(CO_3)_5$, where $(A^{1+}B^{2+}C^{3+})_6$ = $(Na,Ca)_3(Sr,Ba,Ce)_3$ [burbankite]; $Na_3(Ca,Ce,Sr,La)_3$ [calcioburbankite]; $(Na,Ca)_3(Ba,Sr,Ce,Ca)_3$ [khanneshite]; (Na_4Ce_2) [petersenite-(Ce)]; $Na_3(Ce,La,Ca,Na,Sr)_3$ [remondite-(Ce)]; and $Na_3(La,Ce,Ca)_3$ [remondite-(La)]. These diverse compositions hint at the potential combinatorial richness of additional plausible minerals with A^{1+} = Na, K, or NH_4; B^{2+} = Mg, Fe, Mn, Pb, or Ba; and C^{3+} = Y or rare earth elements. All of these rare minerals have been found in association with carbonatites or other alkaline igneous lithologies, which suggests that other examples await discovery in those lithological settings.

Hydrous carbonates

Hydrous carbonates, though volumetrically minor compared to anhydrous carbonates, represent Earth's most chemically and structurally diverse carbon-bearing phases. The 230 approved hydrogen-bearing carbonate minerals occur in more than 100 structure types with as many as 10 coexisting elements, for example in carbokentbrooksite [$(Na,\square)_{12}(Na,Ce)_3Ca_6Mn_3Zr_3NbSi_{25}O_{73}(OH)_3(CO_3)\cdot H_2O$] and johnsenite-(Ce) [$Na_{12}Ce_3Ca_6Mn_3Zr_3WSi_{25}O_{73}(CO_3)(OH)_2$]. Our analysis of synthetic examples in the ICSD database, though limited to compounds with only four or five different elements, yields 38 potential undiscovered minerals (Table 3a). This number is amplified by 53 selected isomorphs of known hydrous carbonate minerals, including several complex phases with six or more elements.

Synthetic hydrous carbonates. The 38 mineral-like synthetic hydrous carbonates with four or five chemical elements listed in Table 3a of necessity incorporate only one or two cations: we list 13 single carbonates and 25 double carbonates. Note that the consideration of synthetic compounds with six or more different elements, including combinations of three or more cations, as well as hydrous carbonates that incorporate halogen elements and/or anionic groups such as $(SO_4)^{2-}$ and $(PO_4)^{3-}$, would significantly increase the list of plausible carbon minerals.

By far the most frequent elements in these phases are alkali metals, with Na, K, and Rb represented by 13, 10, and 6 phases, respectively. The most frequently encountered divalent cations are Co (in 5 compounds) and Ni (4), whereas trivalent Al appears in 3 compounds. Note that hydrous carbonates with Y, rare earth elements, and/or U constitute a significantly greater fraction of synthetic compounds with six or more elements, which are not summarized here.

The 13 mineral-like synthetic single hydrous carbonates include multiple examples of Na, Rb, and Cs phases. Our statistical analysis of known minerals, coupled with the preponderance of synthetic Na phases, suggests that a significant number of sodium carbonates may await discovery. Consider the five approved single carbonate minerals in the system Na-C-O-H: nahcolite ($NaHCO_3$), natron ($Na_2CO_3\cdot 10H_2O$), thermonatrite ($Na_2CO_3\cdot H_2O$), trona [$Na_3(HCO_3)(CO_3)\cdot 2H_2O$], and wegscheiderite [$Na_5H_3(CO_3)_4$]. Missing from this list are two known synthetic compounds, $Na_2CO_3\cdot 1.5H_2O$ (also reported with A^{1+} = K or Rb) and $Na_2CO_3\cdot 7H_2O$, which we suggest are likely to occur naturally as sodium carbonate minerals (Table 3a). These phases, like the other Na carbonates, might be easily overlooked as poorly crystalline and colorless phases (Hazen et al. 2015b). Systematic use of a portable Raman spectrometer at sodium-rich evaporite deposits, such as the salt flats of Lake Natron, Tanzania, might reveal these and other undescribed carbonate minerals.

Three synthetic hydrous single carbonates of divalent cations listed in Table 3a, none of which has a known mineral isomorph, underscore the diversity of potential undiscovered phases. Both $Co_2^{2+}(CO_3)(OH)_2$ and $Pb_2^{2+}O(CO_3)\cdot H_2O$ are not only likely minerals, but they point to numerous plausible mineral isomorphs, as well. The phase $Be^{2+}(CO_3)\cdot xH_2O$ (reported with $x = 4$ in the *Handbook of Chemistry and Physics*) remains enigmatic. It is readily available as a chemical reagent, though its crystal structure is not well characterized. Niveolanite [$NaBeCO_3(OH)\cdot 2H_2O$] is the only known mineral with both Be and C. We suggest that the hydrated Be carbonate might be found in a peralkaline igneous complex such as Mont Saint Hillaire, perhaps as a daughter crystal in fluid inclusions.

The majority of synthetic hydrous carbonates in Table 3a are double carbonates with an alkali metal coupled with a 2+ or 3+ cation. Notable examples that point to plausible minerals include compounds with the general formulas $A_2^{1+}B^{2+}(CO_3)_2\cdot 4H_2O$ with $A^{+1}B^{2+}$ = NaCo, KCo, KNi, RbCo, or RbNi [baylissite, $K_2Mg(CO_3)_2\cdot 4H_2O$, is the sole mineral example]; as well as $A^{1+}B^{2+}H(CO_3)_2\cdot 4H_2O$ with $A^{1+}B^{2+}$ = KMg or KNi; $A_6^{1+}B^{4+}(CO_3)_5\cdot 12H_2O$ with $A^{1+}B^{4+}$ = NaTh or NaCe; and $A^{2+}B^{2+}(CO_3)_2\cdot 3H_2O$ with $A^{2+}B^{2+}$ = MgCr or BaCa.

Hydrous carbonate minerals. The 230 known hydrous carbonate minerals provide the best guide to the potential diversity of yet to be discovered examples. Consider the hydrous single carbonate minerals of divalent cations, including Mg, Ca, Ni, Cu, Zn, and Pb, with the general formula [$A_x^{2+}(CO_3)_y(OH)_{2(x-y)}\cdot nH_2O$]. Known minerals include (*xyn*) = (1,1,0), (1,1,0.4), (1,1,1), (1,1,3), (1,1,5), (1,1,6), (1,1,10), (2,1,1), (2,1,3), (3,1,0), (3,1,4), (3,2,0), (5,2,0), (5,4,5), and (7,2,0). Couple these stoichiometries with synthetic varieties such as (1,1,2) and (2,1,0), as well as oxy-carbonates such as plumbonacrite [$Pb_5(CO_3)_3O(OH)_2$] and synthetic $Pb_2O(CO_3)\cdot 2H_2O$, and the potential combinatoric complexity of "simple" A^{2+}-C-O-H carbonate systems is evident.

Dozens of hydrous carbonate structure types incorporate two cations. Four minerals occur with the general formula $A_2^{1+}B^{2+}(CO_3)_2\cdot nH_2O$: pirssonite [$Na_2Ca(CO_3)_2\cdot 2H_2O$], chalconatronite [$Na_2Cu(CO_3)_2\cdot 3H_2O$], baylissite [$K_2Mg(CO_3)_2\cdot 4H_2O$], and gaylussite [$Na_2Ca(CO_3)_2\cdot 5H_2O$]. Substitution of alternate divalent cations, including (in order of increasing ionic radius) Ni, Mg, Cu, Zn, Co, Fe, Mn, Cd, Ca, Sr, Pb, and Ba, point to numerous possible as yet undescribed isomorphous minerals.

Although most hydrous carbonate mineral formula types are represented by a single species, a few mineral groups incorporate multiple isomorphs. Foremost among these structures, the malachite group includes 10 hydrated carbonate species with the general formula [$A^{2+}B^{2+}(CO_3)(OH)_2$], where $A^{2+}B^{2+}$ equals Cu_2 (malachite), Fe_2 (chukanovite), Ni_2 (nullaginite), Zn_2 (parádsasvárite), Mg_2 (pokrovskite), CuNi (glaukosphaerite), CuCo (kolwezite), CuMg (mcguinnessite), CuZn (rosasite), and ZnCu (zincrosasite). Given that there are at least six known divalent cations in the A and B sites (Ni, Mg, Cu, Zn, Co, and Fe), there exist at least 21 possible AB combinations for malachite group species—more if the larger divalent cations Mn, Cd, or Ca are taken into consideration (Table 3b). Therefore, we anticipate discovery of at least some of the remaining combinatoric possibilities.

Six minerals of the dundasite group of hydrous carbonates have the general formula $A^{2+}B_2^{3+}(CO_3)_2(OH)_4\cdot nH_2O$, where A^{2+} = Ca, Ba, Pb, and Sr, and B^{3+} = Al and Cr. Known examples have $A^{2+}B^{3+}$ = BaAl (dresserite and hydrodresserite; $n = 1.5$), PbAl (dundasite; $n = 1$), CaAl (kochsándorite; $n = 1$), PbCr (petterdite; $n = 1$), and SrAl (strontiodresserite; $n = 1$). These systematics suggest that additional examples with $A^{2+}B^{3+}$ = BaCr, CaCr, and SrCr, as well as possible species with A^{2+} = Ni, Mg, Fe, Mn, and Cd and B^{3+} = Fe, Ti, Mn, and Co, might await discovery (Table 3b).

The hydrotalcite group includes a dozen layered double hydroxide carbonates with varied formulas and several structural variants, most of which conform to $A_4^{2+}B_2^{3+}(OH)_{12}(CO_3)\cdot 3H_2O$ or $A_6^{2+}B_2^{3+}CO_3(OH)_{16}\cdot 4H_2O$ with A^{2+} = Ni, Mg, Zn, Fe, Mn, and Ca, and B^{3+} = Al, Co, Cr, Fe, and Mn. Additional isomorphs might hold A^{2+} = Cu, Co, Sr, Pb, and Ba, and/or B^{3+} = Ti. Given the combinatorially large potential for novel layered minerals, we suggest that several additional examples await discovery (Table 3b).

The ancylite group of rare earth element (REE) carbonates includes seven species with the general formula [$AB(CO_3)_2(OH,H_2O)_2$], where A and B can be a REE (predominantly La, Ce, and Nd) plus Ca, Sr, or Pb. Valid minerals have AB = La_2 [kozoite-(La)], Nd_2 [kozoite-(Nd)], CeSr [ancylite-(Ce)], LaSr [ancylite-(La)], CeCa [calcioancylite-(Ce)], NdCa [calcioancylite-(Nd)], and NdPb [gysinite-(Nd)]. As yet undescribed element combinations, including Ce_2, NdSr, LaCa, CePb, and LaPb, represent possible ancylite isomorphs. Additional phases might incorporate other elements, including Y for REE, and Mn or Ba for Ca, Pb, and Sr (Table 3b).

The remarkable structural and compositional diversity of Y and REE carbonates, with 86 species in more than 50 structure types, points to the probable existence of numerous additional species, including isomorphs of known phases (Table 3b) as well as entirely new structures. Single carbonates occur in the lanthanite mineral group [$A_2^{3+}(CO_3)_3\cdot 8H_2O$], with A^{3+} = Ce, La, and Nd, suggesting the possible natural occurrence of $Y_2(CO_3)_3\cdot 8H_2O$, as well. The other REE single carbonate is calkinsite-(Ce) [$Ce_2(CO_3)_3\cdot 4H_2O$], which could have natural Y, Nd, and La analogs.

Hydrous double carbonates with yttrium or a rare earth element paired with Na or Ca are particularly diverse; examples include shomiokite-(Y) [$Na_3Y(CO_3)_3\cdot 3H_2O$], lecoqite-(Y) [$Na_3Y(CO_3)_3\cdot 6H_2O$], galgenbergite-(Ce) [$CaCe_2(CO_3)_4\cdot H_2O$], kimuraite-(Y) [$CaY_2(CO_3)_4\cdot 6H_2O$], and kamphaugite-(Y) [$Ca_2Y_2(CO_3)_4(OH)_2\cdot 3H_2O$]. Many additional minerals with Y or a rare earth element plus 2 or 3 additional cations are known, including kainosite-(Y) [$Ca_2Y_2(SiO_3)_4(CO_3)\cdot H_2O$], lepersonnite-(Gd) [$CaGd(UO_2)_{24}(CO_3)_8Si_4O_{28}\cdot 60H_2O$] and donnayite-(Y) [$NaSr_3CaY(CO_3)_6\cdot 3H_2O$]. The combinatorial richness of these minerals and their isomorphs arises both from their varied crystal structures and the many combinations of 1+, 2+, 3+, and +4 cations contained therein.

Among the most complex and diverse carbon minerals are 29 hydrous uranium carbonates. Several of these species incorporate [$(UO_2)(CO_3)_3$] groups with +1 (Na, K) and +2 (Mg, Ca) cations. Examples include andersonite [$Na_2Ca(UO_2)(CO_3)_3\cdot 6H_2O$], bayleyite [$Mg_2(UO_2)(CO_3)_3\cdot 18H_2O$], grimselite [$K_3Na(UO_2)(CO_3)_3\cdot H_2O$], ježekite [$Na_8(UO_2)(CO_3)_3(SO_4)_2\cdot 3H_2O$], liebigite [$Ca_2(UO_2)(CO_3)_3\cdot 11H_2O$], línekite [$K_2Ca_3[(UO_2)(CO_3)_3]_2\cdot 7H_2O$], rabbittite [$Ca_3Mg_3[(UO_2)(CO_3)_3]_2(OH)_4\cdot 18H_2O$], and swartzite [$CaMg(UO_2)(CO_3)_3\cdot 12H_2O$]. These systematics suggest numerous additional plausible minerals, both with different arrangements of Na, K, Mg, and Ca, and with additional cations, including the alkali metals Rb and Cs, and divalent Mn, Fe, Co, Ni, Cu, Zn, Sr, Ba, and Pb (Table 3b).

Even greater complexity may exist for U^{6+} carbonates containing Y or rare earth elements, including astrocyanite-(Ce) [$Cu_2Ce_2(UO_2)(CO_3)_5(OH)_2\cdot 1.5H_2O$], bijvoetite-(Y) [$Y_8(UO_2)_{16}O_8(CO_3)_{16}(OH)_8\cdot 39H_2O$], kamotoite-(Y) [$Y_2O_4(UO_2)_4(CO_3)_3\cdot 14H_2O$], lepersonnite-(Gd) [$CaGd_2(UO_2)_{24}(CO_3)_8Si_4O_{28}\cdot 60H_2O$], mckelveyite-(Y) [$NaBa_3(Ca,U)Y(CO_3)_6\cdot 3H_2O$], and shabaite-(Nd) [$CaNd_2(UO_2)(CO_3)_4(OH)_2\cdot 6H_2O$]. Numerous isomorphous phases, as well as new structures, are suggested by this diversity (Table 3b).

Carbonates with halogens

Halogenated carbonates are modestly represented in nature, with 39 F carbonate and 27 Cl carbonate minerals, of which 28 have only four or five constituent chemical elements. We list 24 additional mineral-like synthetic carbonates with F or Cl and up to five different elements, reported in the ICSD database (Table 3a), and thus suggest additional minerals awaiting discovery.

Most synthetic C-O-X^{-1} examples incorporate Ba (eight reported compounds), K (7), Rb (5), rare earth elements (5), Na (4), Pb (3), REE (3), and/or Y (3). Examples of synthetic phases with a single cation include $A_3^{1+}(CO_3)X^{1-}$ with $A^{1+}X^{1-}$ = KF or RbF; $K_3H(CO_3)F\cdot H_2O$; $A_2^{2+}(CO_3)X_2^{1-}$ with $A^{2+}X^{1-}$ = PbBr [also known as natural phases with $A^{2+}X^{1-}$ = CaF (brenkite) and PbCl (phosgenite)]; $Ba_3(CO_3)Cl_4$; and $La(CO_3)F$.

Mineral-like synthetic carbonates with fluorine and two cations exist in at least 11 formula types (Table 3a). Multiple examples occur for $A^{1+}B_2^{1+}(CO_3)F$ with $A^{1+}B^{1+}$ = KRb or RbK; $A^{1+}B^{2+}(CO_3)F$ with $A^{1+}B^{2+}$ = KCa, KSr, RbCa, or RbSr; and $A^{2+}B^{2+}(CO_3)F_2$ with $A^{2+}B^{2+}$ = BaMn, BaCu, or BaZn.

Seven different formula types exist for synthetic and natural compounds in the $[A_x^{2+}B_y^{3+}(CO_3)_zF_{(2x+3y-2z)}]$ system, including (xyz) = (1,1,2), (1,2,3), (2,1,2), (2,1,3), (2,3,5), (3,1,2), and (3,2,5). Most prevalent is the (1,1,2)-type [i.e., $A^{2+}B^{3+}(CO_3)_2F$], including huanghoite-(Ce) and qaqarssukite-(Ce) [both $Ba^{2+}Ce^{3+}(CO_3)_2F$], as well as three minerals of the synchysite group with $A^{2+}B^{3+}$ = CaY [synchysite-(Y)], CaCe [synchysite-(Ce)], and CaNd [synchysite-(Nd)]. These phases suggest the possible occurrence of $A^{2+}B^{3+}$ = CaLa, BaY, BaLa, and BaNd, as well.

The (3,2,5) formula type is known both as synthetic $Ba_3^{2+}La_2^{3+}(CO_3)_5F_2$ and as the mineral cebaite-(Ce) [$Ba_3^{2+}Ce_2^{3+}(CO_3)_5F_2$], which suggests that as yet undocumented natural analogs "cebaite-(Y)," "cebaite-(La)," and "cebaite-(Nd)" await discovery. Note that all of these phases occur with Ca or Ba as the divalent cation and F as the halogen. Variants with Sr or Pb, as well as Cl, are also plausible mineral-like phases.

The combinatorial complexity of isomorphs of the preceding phases is impressive, but is far surpassed by halogenated carbonates that incorporate more than five elements, as represented by such minerals as albrechtschraufite [$Ca_4Mg(UO_2)_2(CO_3)_6F_2\cdot 17H_2O$], ashburtonite [$HPb_4Cu_4(Si_4O_{12})(HCO_3)_4(OH)_4Cl$], bussenite [$Na_2Ba_2Fe^{2+}TiSi_2O_7(CO_3)O(OH)F\cdot H_2O$], carletonite [$KNa_4Ca_4Si_8O_{18}(CO_3)_4(F,OH)\cdot H_2O$], hanjiangite [$Ba_2Ca(V^{3+}Al)(AlSi_3O_{10})(OH)_2]F(CO_3)_2$], and sakhaite [$Ca_{48}Mg_{16}Al(SiO_3OH)_4(CO_3)_{16}(BO_3)_{28}\cdot(H_2O)_3(HCl)_3$].

Carbonates with other anionic groups

Further enriching carbon minerals are carbonates that also contain phosphate, arsenate, borate, silicate, sulfate, and other anionic groups. Few such carbonate phases with five or fewer elements occur; thus Table 3a lists only two synthetic examples. Neither $Y_2(CO_3)_2(C_2O_4)\cdot 2H_2O$ with an oxalate group, nor the lead carbonate-chlorate $Pb_{12}(OH)_{12}(CO_3)(ClO_4)_{10}\cdot 6H_2O$, have known mineral analogs. However, a brief survey of synthetic carbonates with six or seven elements reveals numerous phosphates and sulfates that resemble known minerals.

Fifteen hydrous carbonate minerals incorporate phosphate groups (PO_4). The bradleyite group of carbonate-phosphates includes four described species with the general formula [$Na_3A^{2+}(PO_4)(CO_3)$], with A^{2+} = Fe (bonshtedtite), Mg (bradleyite), Sr (crawfordite), and Mn (sidorenkite). Additional minerals with A^{2+} = Ni, Cu, Zn, Co, Cd, Ca, Pb, and Ba are plausible, as are isomorphs with monovalent K or NH_4 replacing Na (Table 3b).

Twenty-six carbonate-sulfate minerals have been documented. The northupite group [$A_6^{1+}B_2^{2+}(CO_3)_4(SO_4)$] with AB = NaMg, NaFe, and NaMn; burkeite [$Na_4(SO_4)(CO_3)$]; rapidcreekite [$Ca_2(SO_4)(CO_3)\cdot 4H_2O$]; jouravskite [$Ca_3Mn^{4+}(SO_4)(CO_3)(OH)_6\cdot 12H_2O$]; carraraite [$Ca_3Ge(SO_4)(CO_3)(OH)_6\cdot 12H_2O$]; caledonite [$Cu_2Pb_5(SO_4)_3(CO_3)(OH)_6$]; thaumasite [$Ca_3Si(OH)_6(SO_4)(CO_3)\cdot 12H_2O$]; and kegelite [$Pb_4Al_2Si_4O_{10}(SO_4)(CO_3)_2(OH)_4$] exemplify these diverse and chemically complex minerals. As with other carbonates, Na, Mg, and Ca appear most often, but the presence of rarer elements such as Cu, Ge, and Pb suggest that a wide chemical palette should be considered when searching for new C minerals. The coexistence of cations in multiple valence states increases the opportunities for new isomorphous minerals (Table 3b).

A dozen carbon-bearing minerals also incorporate boron, including qilianshanite [$NaH_4(CO_3)(BO_3)\cdot 2H_2O$], canavesite [$Mg_2(HBO_3)(CO_3)\cdot 5H_2O$], borcarite [$Ca_4MgB_4O_6(CO_3)_2(OH)_6$], gaudefroyite [$Ca_4Mn_3^{3+}(BO_3)_3(CO_3)O_3$], and harkerite [$Ca_{12}Mg_4Al(SiO_4)_4(BO_3)_3(CO_3)_5\cdot H_2O$]. As with the previous examples of hydrous carbonates, the structural and chemical complexity of these phases points to numerous plausible isomorphous minerals that have yet to be discovered and described.

Among the other varied carbonates are 52 silicate minerals that incorporate CO_3 groups, though the association of Si with C in minerals is significantly less than might be predicted by these two element's crustal abundances (Hummer et al. 2015). The most common of these carbonate-silicate phases are in the sodalite-cancrinite group of framework silicates, though $(CO_3)^{2-}$ groups are not essential to all species. Silicate-carbonates notably include orthosilicates such as galuskinte [$Ca_7(SiO_4)_3(CO_3)$] and spurrite [$Ca_5(SiO_4)_2(CO_3)$], as well as silicates with Si_2O_7 dimers such as biraite-(Ce) [$Ce_2Fe^{2+}Si_2O_7(CO_3)$] and tilleyite [$Ca_5Si_2O_7(CO_3)_2$], which are known principally from contact metamorphic skarn zones between carbonate formations and igneous intrusives. Layer silicates are also represented, for example niksergievite [$Ba_2Al_3(Si,Al)_4O_{10}(CO_3)(OH)_6\cdot nH_2O$] and surite [$(Pb,Ca)_3Al_2(Si,Al)_4O_{10}(CO_3)_2(OH)_3\cdot 0.3H_2O$], which attest to the structural diversity of these relatively rare C-Si phases.

Carbonate minerals also occasionally incorporate what might be considered to be atypical anionic groups. Thiosulfate $(S_2O_3)^{2-}$ groups are much less common in minerals than sulfate $(SO_4)^{2-}$ groups in today's oxidized near-surface environment. Nevertheless, one carbonate-thiosulfate mineral, fassinaite [$Pb_2^{2+}(CO_3)(S_2O_3)$], is known. This oddity points to the possibility that other such phases might exist, or perhaps occurred more extensively during an earlier period of Earth history when more reducing conditions prevailed.

The diverse inventory of hydrous carbonate minerals also includes three arsenates, one molybdate, and three tellurates. However, in spite of the great structural and compositional diversity of carbonates, there are as yet no known carbon minerals that incorporate selenate or antimonate anionic groups, nor have the cations Rb, Sn, Cs, Ag, Au, Tl, or platinum group elements been found to coexist naturally as essential mineral-forming elements with C. Perhaps these "missing" chemical classes of natural carbon compounds present additional opportunities for mineralogical discovery. Unusual juxtapositions of elements do occur on Earth, and we should expect some chemical surprises in yet to be discovered carbon-bearing minerals.

SEARCHING FOR NEW CARBON MINERALS

Hazen et al. (2015a) suggested that every mineral-forming element has the potential to form at least 1000 mineral species, even if only a fraction of those potential minerals exist on Earth today. The case of carbon mineral diversity supports this prediction. In this contribution we list 242 mineral-like synthetic compounds with two, three, four, or five different chemical elements, as well as 190 potential isomorphs of known minerals. Given crystal chemical principles and the combinatorial richness of known carbon compounds, one could easily catalog more than 1000 plausible carbon-bearing minerals.

Given our detailed knowledge of the diversity and distribution of existing mineralogical examples, it is possible to predict promising localities to look for Earth's as yet undiscovered carbon minerals. Two complementary strategies facilitate this search: reexamination of Earth's most prolific carbon mineral localities, and a survey of the varied occurrences of carbon minerals.

Earth's most diverse carbon mineral localities

Table 4 summarizes data on the 14 mineral localities with the greatest known diversity of carbon-containing minerals based on information provided by mindat.org. Each of these localities features 20 or more C-bearing species, many of which are rare. New carbon-bearing minerals undoubtedly remain to be discovered at these prolific localities.

The Poudrette Quarry within the nepheline syenite complex of Mont Saint-Hilaire, Québec, Canada, holds the record of 78 different carbon-bearing minerals. Twenty-two of these species were discovered there, 12 of which are unique to the Poudrette Quarry. This remarkable diversity of rare minerals arises in part from the complex initial chemistry of the Mont Saint-Hilaire alkaline igneous complex, leading to late-stage concentration of incompatible elements such as B, Ba, Be, F, Mn, Nb, P, REE, Sr, Ti, W, Y, and Zr, and correspondingly rich primary mineralization (Currie et al. 1986; Schilling et al. 2011). Dozens of additional rare phases formed subsequently through aqueous alteration and oxidation. An obvious strategy, therefore, is to scrutinize new and existing specimens from those rich deposits for previously overlooked phases. One such opportunity is to focus on Sr-bearing carbonates. Numerous plausible examples can be proposed (Tables 3a and 3b), yet only 21 species are now known, 11 of which have been documented from Mont Saint-Hilaire and two of which are type specimens: calcioburbankite [$Na_3(Ca,Ce,Sr,La)_3(CO_3)_5$] and donnayite-(Y) [$NaSr_3CaY(CO_3)_6 \cdot 3H_2O$]. Furthermore, this locality has yielded 8 of the 11 known carbonate minerals in which Sr combines with Y or REE. Thus, new Sr-Y/REE minerals might be discovered through systematic examination of museum samples that contain other Sr carbonates.

Other localities with significant diversity of carbon minerals also feature alkali igneous intrusives, notably at the Khibiny Massif in Russia (43 species, four of which are type species; Zaitsev et al. 1998; Yakovenchuk et al. 2005); the Vouriyarvi Massif, also in Russia (25 species; type locality for three species; Zaitsev et al. 1996); and the Francon Quarry, Montréal, Québec, Canada (21 species; type locality for seven species; Tarassoff et al. 2006). These localities reveal various alkaline carbonates, as well as numerous rare minerals with Nb, Ti, and Zr (Steacy and Jambor 1969). Of special interest at the Khibiny Massif are three (of the four known) titanium-REE silicate-carbonates: tundrite-(Ce) [$Na_2Ce_2TiO_2SiO_4(CO_3)_2$], bussenite [$Na_2Ba_2Fe^{2+}TiSi_2O_7(CO_3)O(OH)F \cdot H_2O$], and kihlmanite-(Ce) [$Ce_2TiO_2(SiO_4)(HCO_3)_2 \cdot H_2O$]. The latter two of these minerals are unique to the Khibiny Massif. We suggest that additional examples of Ti carbonates might be found in association with these phases.

Most of the other localities with exceptional diversity of carbon minerals are polymetallic ore bodies that have been subjected to aqueous alteration and oxidative weathering. The Clara Mine in Baden-Wurttemberg, Germany (Bucher et al. 2009; Pfaff et al. 2012) is the richest of these deposits, holding 37 reported species associated with gneiss- and sandstone-hosted barite and fluorite veins. Both Na and alkaline earth carbonates with Bi, Cu, Fe, Mn, Pb, REE, U, and Zn, including the new mineral claraite [$Cu^{2+}_3(CO_3)(OH)_4 \cdot 4H_2O$], have been described from this locality.

Two localities in north-central Namibia have produced diverse C minerals, including several significant new species. The unique dolomite-hosted Cu-Pb-Zn-Ag-Ge-Cd mineralized zones of Tsumeb, Namibia (Wilson 1977; Bowell 2014) boast 29 carbon mineral species, including several rare carbonates of Ca, Cd, Cu, Fe, Mn, Pb, and Zn. Among the many type minerals from Tsumeb are otavite ($CdCO_3$) of the calcite group and minrecordite [$CaZn(CO_3)_2$] of the dolomite group. The nearby Kombat Mine (Innes and Chaplin 1986; Dunn 1991), though less well known than Tsumeb, hosts 20 different carbon minerals, many of which occur in Mn-Pb-Cu mineralized zones near dolostone. Unusual Mn carbonates at the Kombat Mine include the first known occurrence of holdawayite [$Mn^{2+}_6(CO_3)_2(OH)_7(Cl,OH)$]. The Jáchymov mining district in the Karlovy Vary region of the Czech Republic (Ondrus et al. 2003a, 2003b) also displays dolomite-hosted ore deposits. The Ag-Co-Ni-Bi-U mineralization leads to 36 C mineral species, including the only reported occurrence of albrechtschraufite [$Ca_4Mg(UO_2)_2(CO_3)_6F_2 \cdot 17H_2O$] and the rare mineral čejkaite [$Na_4UO_2(CO_3)_3$].

Two contrasting localities in the United States hold at least 20 different C-bearing mineral species. The Bisbee, Arizona porphyry copper deposits are hosted by Paleozoic calcareous sediments that were intruded by Jurassic stocks, dikes, and sills, and associated mineralizing fluids rich in Cu, Ag, Au, Pb, and Zn (Ransome 1904; Bryant and Metz 1966). Although no new carbon minerals have been described from Bisbee, the extent of Cu, Fe, Pb, and Zn carbonates constituting important ores is remarkable.

The limestone-hosted Zn-Fe-Mn ore bodies of the Franklin/Sterling Hill district in Sussex County, New Jersey (Palache 1937) are notable for their varied carbonates of Cu, Fe, Mn, and Zn. The first stages of complex carbonate mineralization occurred as a consequence of granitic intrusions, and associated development of contact metamorphic skarns and pegmatite minerals. Subsequent pulses of mineralizing fluids, including remobilization of As and the formation of varied arsenate minerals, contributed to the great mineralogical diversity of Franklin. Among the numerous minerals first described from this district is the only occurrence of the Fe-Zn hydrous carbonate-sulfate hauckite [$Fe^{3+}_3Mg_{24}Zn_{18}(SO_4)_4(CO_3)_2(OH)_{81}$].

The metamorphosed Mn-Fe deposits of Långban, Sweden, which feature complex mineralogy associated with skarns and pegmatites (Holtstam and Langhof 1999; Jonsson and Broman 2002), display several mineralogical similarities to the Franklin district. Långban has yielded 22 C-bearing minerals, of which five were new carbonate species at the time of description:

TABLE 4. Mineral localities with the greatest diversity of carbon minerals, their lithological settings, and the principal mineral-forming elements

Locality	No. of C minerals	Lithological context	Key carbonate elements
Poudrette Quarry, Mont Saint-Hilaire, Québec, Canada	78	Alkaline intrusion, nepheline syenite	Ba, Ca, Cu, K, Mn, Na, P, Pb, REE, Sr, Th, Y, Zn, Zr
Kukisvumchorr Mt, Khibiny Massif, Kola Peninsula, Russia	43	Alkaline intrusion with carbonatite	Ba, Ca, Cu. Fe, Mg, Mn, Na, REE, Sr, Ti
Clara Mine, Wolfach, Baden-Wurttemberg, Germany	37	Gneiss- and sandstone-hosted barite-fluorite veins	B, Bi, Ca, Cu, Fe, K, Mg, Mn, Pb, REE, U, Zn
Jáchymov, Karlovy Vary Region, Bohemia, Czech Republic	36	Ag-Co-Ni-Bi-U ore body	Ca, Cu, Fe, Mg, Mn, Na, Pb, REE, U, Y, Zn
Tsumeb Mine, Tsumeb, Namibia	29	Dolomite-hosted Cu-Pb-Zn-Ag-Ge-Cd ore body	Ca, Cd, Cu, Fe, Mn, Pb, Zn
Vuoriyarvi Massif, Northern Karelia, Russia	25	Alkaline intrusion; ultrabasic	Ba, Ca, Fe, K, Na, REE, Sr, Y
Sounion Mine No. 19, Attikí Prefecture, Greece	24	Granodiorite-hosted Zn-Pb-Cu-Ag ore body	Bi, Cu, Fe, Ni, Pb, Zn
Friedrichssegen Mine, Rhineland-Palatinate, Germany	23	Devonian schist-hosted Zn-Pb-Cu-Ag ore body	Cu, Mn, Pb, Zn
Långban, Filipstad, Värmland, Sweden	22	Metamorphosed Mn-Fe deposit with skarns and pegmatites	B, Ba, Cu, Fe, Mn, Pb
Bisbee, Warren District, Mule Mts, Cochise Co., Arizona, U.S.A.	22	Limestone-hosted Cu-Ag-Au-Pb-Zn ore body	B, Bi, Cu, Pb, Zn
Francon Quarry, Montréal, Québec, Canada	21	Alkali intrusive complex	Ba, P, Pb, REE, Sr, Th, Ti, U, Zr
Glücksrad Mine, Oberschulenberg, Harz, Germany	20	Pb-Zn-Cu ore body	Cu, Pb, Zn
Kombat Mine, Grootfontein District, Namibia	20	Mn-Pb-Cu mineralization	B, Cu, Mn, Pb
Sterling Mine, Sussex Co., New Jersey, U.S.A.	20	Limestone-hosted Zn ore body	Cu, Fe, Mn, Zn

britvinite [$Pb_{14}Mg_9Si_{10}O_{28}(BO_3)_4(CO_3)_2F_2(OH)_{12}$], hydrocerrusite [$Pb_3(CO_3)_2(OH)_2$], molybdophyllite {$Pb_8Mg_9[Si_{10}O_{30}(OH)_8(CO_3)_3]\cdot H_2O$}, pyroaurite [$Mg_6Fe^{3+}_2CO_3(OH)_{16}\cdot 4H_2O$], and philolithite [$Pb_{12}O_6Mn(Mg,Mn)_2(Mn,Mg)_4(SO_4)(CO_3)_4Cl_4(OH)_{12}$]. As with several others of Earth's richest mineral localities, Långban experienced several pulses of mineralizing fluids of different temperatures and compositions, each of which added to the diversity of the deposit.

Mineral occurrence data

A second strategy for identifying promising localities for the discovery of new carbon minerals involves examination of the "Occurrence" data for each of the 258 carbon-bearing minerals (220 of which are carbonates) in Volume V of the *Handbook of Mineralogy* (*HoM*; Anthony et al. 2003), as well as published occurrence information for selected minerals. *HoM* provides a description of geological settings and physical and chemical environments for each species, and thus points to the most likely lithological contexts for the discovery of new minerals.

Occurrences of carbides and organic minerals are discussed in previous sections; here we focus on carbonate minerals. Several geological settings dominate the occurrences of rare carbonate minerals: varied alkali igneous intrusive lithologies, including carbonatite-bearing alkaline massifs; carbonate rocks subjected to contact metamorphism; rocks altered by carbonated hydrothermal systems; and oxidized zones of ore deposits. These occurrences echo the parageneses of Earth's 14 most prolific carbon mineral localities (Table 4).

Alkali intrusive igneous rocks host at least 39 carbonate species, most of which contain alkali cations plus Y or rare earth elements (REE). Nepheline syenite (notably Mont Saint-Hilaire), alkali massifs (including the Vuoriyarvi and Khibiny massifs in Russia), and varied intrusives, including ultrabasic cumulates, olivine basalt, sodalite syenite, and alkali granites, have been found to host rare species. Several unusual phases appear to be restricted to the late-stage pegmatitic phases of these igneous complexes (London 2008); examination of specimens from these deposits, including study of possible crystalline phases in fluid inclusions, might reveal new hydrous carbonate minerals.

Carbonatites, which are rare igneous rocks comprised largely of carbonate minerals (Jones et al. 2013), are reported as the principal occurrence of 26 carbonate minerals in the *Handbook of Mineralogy*. As with rocks derived from alkali silicate melts, many of these carbonatite phases incorporate an alkali metal plus yttrium or rare earth elements, and point to the likelihood of as yet unrecognized minerals of similar chemistry. Discovery of new species is complicated by the fact that many of these phases may be colorless, poorly crystalized, and/or microscopic. Nevertheless, scrutiny of new or existing specimens from such fertile carbonatite deposits as Oldoinyo Lengai, Tanzania (the only active carbonate volcano), and rare earth element mining districts such as the Oka Carbonatite, Québec, Canada; Bayan Obo, Mongolia; Panda Hill, Tanzania; and Palabora, South Africa, is warranted (Jones et al. 2013).

More than 30 rare hydrous carbonate minerals arise from the apparent interaction of carbonated hydrothermal fluids with prior minerals, including ore deposits concentrated in Au-Te [mroseite; $CaTe^{4+}O_2(CO_3)$], Bi [beyerite; $CaBi_2O_2(CO_3)_2$], U [oswaldpeetersite; $(UO_2)_2CO_3(OH)_2\cdot 4H_2O$], and Y [tengerite-(Y); $Y_2(CO_3)_3\cdot 2–3H_2O$]. Closely related to these occurrences are more than 70 carbonates that have been found in the oxidized weathering zones of ore bodies. These phases include familiar hydrous carbonates such as azurite [$Cu_3(CO_3)_2(OH)_2$], malachite [$Cu_2CO_3(OH)_2$], and zaratite [$Ni_3CO_3(OH)_4\cdot 4H_2O$], as well as numerous rare minerals of Co, Ni, Cu, Zn, Hg, Pb, and U (including 21 uranyl carbonates). Continued examations of ore bodies altered by oxidation and/or late-stage hydrothermal activity are sure to yield new carbonate minerals.

Significant diversity of rare carbonate minerals, especially carbonate-silicate species, occurs in skarns—the contact metamorphic zones of limestone or dolostone with igneous intrusives. A characteristic locality is Crestmore in Riverside County, California, where Mississippian Mg-rich limestones have been intruded by quartz diorite and quartz monazite porphyry. Though not in the list of localities with the greatest C-mineral diversity, the Crestmore Quarries are notable as the type locality of tilleyite [$Ca_5Si_2O_7(CO_3)_2$], in association with five other Ca-Si carbonates.

Added to these igneous and contact metamorphic occurrences of rare carbonate minerals are several paragenetic modes related to sediments that lead to mineralogical novelties. The dominant forms of sedimentary carbonates are as primary chemical precipitates (notably calcite), but also evaporites (such as the hydrous Na carbonates) and fumerolic deposits [e.g., chlorartinite, $Mg_2CO_3Cl(OH)\cdot 2.5H_2O$; and giorgiosite, $Mg_5(CO_3)_4(OH)_2\cdot 5H_2O$]. Several carbonates, as well as oxalates and other organic minerals, are associated with soils and C-rich detrital sedimentary formations. Soil minerals range in context from ocean floor [earlandite, $Ca_3(C_6H_5O_7)_2\cdot 4H_2O$] and hypersaline lake sediments [scarbroite, $Al_5(CO_3)(OH)_{13}\cdot 5H_2O$], to peat [weddellite, $CaC_2O_4\cdot 2H_2O$], oil shale [abelsonite, $NiC_{31}H_{32}N_4$], pyritic shale [kratochvilite, $C_{13}H_{10}$], and coal (more than a dozen C minerals).

Finally, carbon minerals occur in a remarkable variety of unexpected contexts: the acetate mineral calclacite [$Ca(CH_3COO)Cl\cdot 5H_2O$] is known exclusively as crystals on limestone samples that interact with acetate from oak museum drawers; bütschilite [$K_2Ca(CO_3)_2$] is known primarily from the ash of trees struck by lightning; and chalconatronite [$Na_2Cu(CO_3)_2\cdot 3H_2O$] and barstowite [$Pb_4CO_3Cl_6\cdot H_2O$] have been recorded as reaction products on archeological artifacts of bronze and lead, respectively. Thus, the keen-eyed mineralogist must cast a wide net in the search for as yet undiscovered carbon minerals.

IMPLICATIONS

In the search for "Earth-like" planets, perhaps the most significant geochemical considerations are a dynamic carbon cycle coupled to a hydrosphere—both essential factors in Earth's evolving biosphere. The mineralogical richness of Earth's near-surface environment is a direct consequence of biology; however, the origin of life may be equally dependent on the chemical environments fostered by near-surface mineral diversity (Hazen 2006; Cleaves et al. 2012). What factors lead to the rich diversity of carbon minerals found on Earth? To what extent does chance vs. necessity play roles in this diversification (Grew and Hazen 2014; Hazen et al. 2015a)?

On the one hand, the diversity of carbon minerals closely follows predictions based on the crustal abundances of elements (Yaroshevsky and Bulakh 1994; Higgins and Smith 2010; Christy 2015; Hazen et al. 2015a); elements with greater crustal abundances tend to display correspondingly greater numbers of mineral species. The 403 documented carbon mineral species are thus consistent in diversity with the estimated 3240 ppm upper continental crustal abundance of C (Wedepohl 1995).

Note, however, that other "Earth-like" planets—those with similar radius, density, and orbital parameters—may have significantly greater carbon abundances than Earth for at least two reasons. First, Earth may have lost a significant fraction of its near-surface carbon during the catastrophic Moon-forming impact event (Sleep et al. 2014). Other terrestrial planets around Sun-like stars may thus have a significantly greater crustal C abundance and a correspondingly greater potential for carbon mineral diversity.

A second consideration, potentially of much greater significance, is the large variation in major element compositions of extrasolar planets. Recent studies of stellar stoichiometry, which rely on quantitative analysis of spectra from relatively nearby stars, reveal a population of star systems with $C/O > 1$ (Delgado et al. 2010; Madhusudhan et al. 2011; Nissen 2013; Young et al. 2014), compared to $C/O \sim 0.076$ for our Solar System (based on CI chondrites; Wedepohl 1995). Furthermore, observations of the most ancient galaxies—those formed within the first 2 billion years of the Big Bang—suggest that the earliest populations of stars were especially enriched in carbon (Maiolino et al. 2015). Significant variations are also observed in other element ratios in stars, including Mg/Si and Fe/O. Although elemental abundances in stars will not generally match those in their associated planets (a consequence, for example, of chemical fractionation during nebular evolution), such large differences in major element ratios may have profound effects on planetary mineralogy. Thus, for example, Bond et al. (2010) modeled a planet orbiting HD 19994 with $C/O = 0.78$, compared to ~0.003 for the bulk Earth (McDonough and Sun 1995). Analysis of the probable mineralogy of such a planet (Unterborn et al. 2014) points to a diamond-rich mantle in which convection is sluggish or absent, thus potentially restricting the planet's carbon cycle.

These mineralogical considerations underscore uncertainties in what we should consider to be an "Earth-like" planet. Many planets may possess similar radius and density, combined with stable orbits in a star's habitable zone. However, if major element ratios of a planet are significantly different from those of Earth, then that planet's predominant rock-forming minerals will likely differ from Earth's, as well—differences that can impact planetary dynamics and evolution. Therefore, we suggest that for a planet to be considered to be Earth-like it should possess the same common rock-forming minerals, including the carbonates of Mg, Ca, Mn, and Fe.

Earth's carbon minerals reveal another, more subtle aspect of "Earth-like." On the one hand, we are justified in seeking worlds that mimic our own—worlds that might host similar mineral and biological richness. The discovery of such a planet, and the attendant realization that we are not alone in the cosmos, would transform our understanding of our place in the universe. Nevertheless, given the large number of rare carbon-bearing mineral species, more than 100 of which are known from only one locality, Earth's mineralogy is demonstrably unique (Hystad et al. 2015b). Thus, in spite of the ongoing quest to find a convincing planetary sibling, it is also satisfying to know that Earth has been, and will continue to be, unique in the cosmos.

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