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Chromium mineral ecology

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ABSTRACT

Minerals containing chromium (Cr) as an essential element display systematic trends in their diversity and distribution. We employ data for 72 approved terrestrial Cr mineral species (http://rruff.info/ima, as of 15 April 2016), representing 4089 mineral species-locality pairs (http://mindat.org and other sources, as of 15 April 2016). We find that Cr-containing mineral species, for which 30% are known at only one locality and more than half are known from three or fewer localities, conform to a Large Number of Rare Events (LNRE) distribution. Our model predicts that at least 100 ± 13 (1σ) Cr minerals exist in Earth's crust today, indicating that 28 ± 13 (1σ) species have yet to be discovered—a minimum estimate because our model assumes that new minerals will be found only using the same methods as in the past. Numerous additional Cr minerals likely await discovery using micro-analytical methods.

We propose 117 compounds as plausible Cr minerals to be discovered, including 7 oxides, 11 sulfides, 7 silicates, 7 sulfates, and 82 chromates. Depending on their compositions and crystal structures, new Cr minerals are likely to be discovered in various environments, including meteorites, basalt, evaporites, and oxidized Pb ore deposits.

Keywords: Chromium, mineral ecology, new minerals, statistical mineralogy

INTRODUCTION

Newly discovered mineral species have been an important focus of descriptive mineralogy. As mineral discovery becomes more difficult, it is useful to predict the number, nature, and localities of undiscovered minerals on Earth. Mineral ecology, which couples large mineralogical data resources (Hazen et al. 2015a, 2015b; Hystad et al. 2015a, 2015b) with statistical methods developed from ecology and lexicology (Baayen 2001; Evert and Baroni 2008), is now leading to predictions of Earth's "missing" minerals (Hazen et al. 2016; Grew et al. 2016).

This study is focused on the ecology of Cr mineral species. Cr is a redox-sensitive first-row transition element that is of special interest because of its strategic importance (National Research Council 2008; Orcutt 2011) and environmental impact (Katz and Salem 1994; Pellerin and Booker 2000), as well as its critical roles in biology (Mertz 1969). Cr is a very common minor element in the crust, averaging ~138 ppm crustal abundance (Rudnick and Gao 2005), with upper crustal abundance of ~97 ppm (Rudnick and Gao 2005) and lower crustal abundance of ~215 ppm (Rudnick and Fountain 1995). Cr concentrations vary significantly among different rock types, ranging from ~20 ppm in granitic rocks, ~200 ppm in basaltic rocks, and to ~2000 ppm in ultramafic rocks (Henderson 1982; Allard 1995). While Cr is a common trace element in many rock-forming minerals (e.g., Duke 1976), it is also found as an essential element in 82 minerals (http://rruff.info/ima as of 1 March 2016; Lafuente et al. 2015). The limited number of species makes it possible to complete a comprehensive survey of Cr mineral species and their localities. A subsequent contribution will focus on the temporal distribution and tectonic settings of Cr minerals.

THE MINERALS OF CHROMIUM

Of all 82 Cr minerals currently discovered, 72 of them occur in terrestrial rocks (Table 1a), 15 species were discovered in meteorites (Table 2a), and 5 species were reported in both. Terrestrial Cr minerals are composed of 39 Cr^{3+} and 26 Cr^{6+} species, in addition to 3 Cr metals/alloys and 4 minerals with undetermined Cr charges. Cr^{3+} minerals are mostly abiotic. Cr^{3+} occupies the octahedral sites of many minerals (e.g., spinel, garnet, tourmaline) by substituting for Fe^{3+}, Mg^{2+}, Ca^{2+}, Al^{3+}, or Ti^{4+}. Therefore, the Cr^{3+} minerals exhibit various crystal structures, and occur in a broad range of environments, from igneous rocks (typical minerals: chromite, magnesiochromite), metamorphic rocks (typical minerals: uvarovite, eskolaite), to hydrothermal veins (typical mineral: uvarovite). Cr^{6+} minerals are mostly biotic sensu lato, i.e., their occurrences are due to oxidation of Earth's surface, which is in turn related to bioactivity. Cr^{6+} minerals can be found in evaporites (typical mineral: lopezite) and oxidized lead deposits (typical mineral: crocoite). The 7 terrestrial Cr minerals containing neither Cr^{3+} nor Cr^{6+} are 3 metals/alloys, 2 carbides, and 2 sulfides, occurring in igneous or metamorphic rocks or in weathered meteorites. Cr minerals found in both meteorites and terrestrial rocks include

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TABLE 1a. IMA recognized terrestrial minerals of chromium, with numbers of recorded occurrences in parentheses (see text), chemical formulas, paragenetic modes, Cr charge, and selected mineral localities (see Table 1b for key to localities)

No.	Name (No. of localities)	Formula	Paragenetic mode[a]	Cr Charge	Biotic	Localities
1	Chromferide (2)	$Fe_{1.5}Cr_{0.2}$	5	0		17
2	Chromium (14)	Cr	5	0		17, 19
3	Ferchromide (2)	$Cr_{1.5}Fe_{0.2}$	5	0		17
4	Bentorite (1)	$Ca_6Cr_2(SO_4)_3(OH)_{12}\cdot 26H_2O$	5	3		4
5	Bracewellite (2)	$CrO(OH)$	6	3		6
6	Chromceladonite (1)	$KMgCrSi_4O_{10}(OH)_2$	3	3		11
7	Chromio-pargasite (1)	$NaCa_2(Mg_4Cr)(Si_6Al_2)O_{22}(OH)_2$	7	3	X	12
8	Chromite (3054)	$FeCr_2O_4$	1, 2, 9	3		1, 5, 8, 12, 18
9	Chromium-dravite (8)	$NaMg_3Cr_6(Si_6O_{18})(BO_3)_3(OH)_3OH$	3	3		8, 11
10	Chromo-alumino-povondraite (2)	$NaCr_3(Al_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$	3	3		1
11	Chromphyllite (4)	$KCr_2(Si_3Al)O_{10}(OH)_2$	3	3		1, 8, 11
12	Cochromite (3)	$CoCr_2O_4$	3	3		21
13	Cuprokalininite (1)	$CuCr_2S_4$	3	3		1
14	Eskolaite (19)	Cr_2O_3	3	3		1, 6, 8, 18, 27
15	Florensovite (1)	$Cu(Cr_{1.5}Sb_{0.5})S_4$	3	3		1
16	Grimaldiite (4)	$CrO(OH)$	5	3		6, 7
17	Guyanaite (2)	$CrO(OH)$	3	3		6
18	Hawthorneite (2)	$BaMgTi_3Cr_4Fe_2Fe_2O_{19}$	3	3		32
19	Kalininite (2)	$ZnCr_2S_4$	3	3		1, 21
20	Knorringite (3)	$Mg_3Cr_2(SiO_4)_3$	1	3		5
21	Kosmochlor (8)	$NaCrSi_2O_6$	1, 9	3		1
22	Magnesiochromite (285)	$MgCr_2O_4$	1	3		1, 5, 12, 13, 19
23	Manganochromite (6)	$MnCr_2O_4$	3	3		21
24	Mariinskite (1)	$BeCr_2O_4$	3	3		18
25	Mcconnellite (2)	$CuCrO_2$	5	3		6
26	Olkhonskite (1)	$Cr_2Ti_3O_9$	3	3		27
27	Oxy-chromium-dravite (1)	$NaCr_3(Cr_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$	3	3		1
28	Petterdite (2)	$PbCr_2(CO_3)_2(OH)_4\cdot H_2O$	7	3	X	3, 7
29	Polyakovite- (Ce) (1)	$(Ce,Ca)_4MgCr_2(Ti,Nb)_2Si_4O_{22}$	3	3		26
30	Putnisite (2)	$SrCa_4Cr_8(CO_3)_8SO_4(OH)_{16}\cdot 25H_2O$	6	3		35
31	Redledgeite (4)	$Ba(Ti_6Cr_2)O_{16}$	5	3		5
32	Redingtonite (2)	$FeCr_2(SO_4)_4\cdot 22H_2O$	7	3	X	30
33	Rilandite (1)	$Cr_6SiO_{11}\cdot 5H_2O$	8	3	X	33
34	Shuiskite (3)	$Ca_2MgCr_2(SiO_4)(Si_2O_7)(OH)_2\cdot H_2O$	3, 7	3		13
35	Stichtite (44)	$Mg_6Cr_2CO_3(OH)_{16}\cdot 4H_2O$	7	3	X	4, 7, 13, 20
36	Uvarovite (208)	$Ca_3Cr_2(SiO_4)_3$	3, 5, 7	3		1, 5, 8, 12, 13
37	Vanadio-oxy-chromium-dravite (1)	$NaV_3(Cr_4Mg_2)(Si_6O_{18})(BO_3)_3(OH)_3O$	3	3		1
38	Verbierite (1)	$BeCr_2TiO_6$	7	3		38
39	Volkonskoite (20)	$Ca_{0.3}(Cr,Mg)_2(Si,Al)_4O_{10}(OH)_2\cdot 4H_2O$	6, 7, 8	3	X	4
40	Woodallite (7)	$Mg_6Cr_2(OH)_{16}Cl_2\cdot 4H_2O$	7	3	X	20
41	Yedlinite (1)	$Pb_6CrCl_6(O,OH,H_2O)_8$	6	3	X	2
42	Yimengite (3)	$K(Cr,Ti,Fe,Mg)_{12}O_{19}$	3	3		25
43	Zincochromite (5)	$ZnCr_2O_4$	3	3		11
44	Cassedanneite (2)	$Pb_5(VO_4)_2(CrO_4)_2\cdot H_2O$	7	6	X	31
45	Chromatite (4)	$CaCrO_4$	6	6	X	4
46	Chrombismite (12)	$Bi_{16}CrO_{27}$	5	6	X	29
47	Chromschieffelinite (1)	$Pb_{10}Te_6O_{20}(OH)_{14}(CrO_4)\cdot 5H_2O$	7	6	X	23
48	Crocoite (86)	$PbCrO_4$	7	6	X	2, 3, 7, 9, 10
49	Deanesmithite (1)	$Hg_2Hg_3S_2OCrO_4$	7	6	X	22
50	Dietzeite (4)	$Ca_2(IO_3)_2CrO_4\cdot H_2O$	6	6	X	14
51	Dukeite (2)	$Bi_{24}Cr_8O_{57}(OH)_6\cdot 3H_2O$	7	6	X	29
52	Edoylerite (1)	$Hg_3(CrO_4)S_2$	7	6	X	22
53	Embreyite (4)	$Pb_5(CrO_4)_2(PO_4)_2\cdot H_2O$	7	6	X	3
54	Fornacite (86)	$CuPb_2(CrO_4)(AsO_4)(OH)$	7	6	X	2, 3, 15, 16, 23
55	George-ericksenite (1)	$Na_6CaMg(IO_3)_6(CrO_4)_2\cdot 12H_2O$	6	6	X	37
56	Georgerobinsonite (1)	$Pb_4(CrO_4)_2(OH)_2FCl$	7	6	X	2
57	Hashemite (1)	$BaCrO_4$	6	6	X	4
58	Hemihedrite (13)	$Pb_{10}Zn(CrO_4)_6(SiO_4)_2F_2$	7	6	X	9, 10, 15, 16
59	Iquiqueite (2)	$K_3Na_4Mg(CrO_4)B_{24}O_{39}(OH)\cdot 12H_2O$	6	6	X	14
60	Iranite (11)	$Pb_{10}Cu(CrO_4)_6(SiO_4)_2(OH)_2$	7	6	X	2, 15, 16
61	Lopezite (5)	$K_2Cr_2O_7$	6	6	X	14
62	Macquartite (1)	$Cu_2Pb_7(CrO_4)_4(SiO_4)_2(OH)_2$	7	6	X	2
63	Phoenicochroite (37)	$Pb_2O(CrO_4)$	7	6	X	2, 3, 9, 10, 15
64	Reynoldsite (2)	$Pb_2Mn_2O_5(CrO_4)$	7	6	X	7
65	Santanaite (1)	$Pb_{11}CrO_{16}$	7	6	X	36
66	Tarapacaite (3)	K_2CrO_4	6	6	X	14
67	Vauquelinite (64)	$CuPb_2(CrO_4)(PO_4)(OH)$	7	6	X	2, 3, 9, 10, 23
68	Wattersite (2)	$Hg_4HgO_2(CrO_4)$	7	6	X	22
69	Cronusite (1)	$Ca_{0.2}CrS_2\cdot 2H_2O$	9	x		39
70	Isovite (1)	$(Cr,Fe)_{23}C_6$	6	x		28
71	Tongbaite (2)	Cr_3C_2	1	x		19, 28
72	Yarlongite (1)	$Cr_4Fe_4NiC_4$	7	x	X	34

Notes: This table includes only minerals with Cr occupying more than 50% of a symmetrically distinct crystallographic site (except for the alloy mineral chromferide, which is recognized as a mineral because of the presence of ~11 at% Cr). Mineral and locality data were compiled from MinDat.org as of April 15, 2016. [a] Paragenetic Mode: 1 = Intrusive igneous; 3 = Metamorphic; 5 = Hydrothermal; 6 = Sedimentary; 7 = Weathering; 8 = Biologically Mediated; 9 = Meteorites.

Table 1b. Mineral localities with the greatest diversity of Cr minerals, number and identity of Cr minerals, their lithological settings

No.	Locality
1	Pereval Marble Quarry, Slyudyanka (Sludyanka), Lake Baikal Area, Irkutskaya Oblast', Prebaikalia (Pribaikal'e), Eastern-Siberian Region, Russia
2	Mammoth-Saint Anthony Mine (Mammoth-St Anthony Mine; Mammoth Mine; St. Anthony Mine), St. Anthony Deposit, Tiger, Mammoth District, Pinal Co., Arizona, U.S.A.
3	Callenberg North Open Cut (No. 1), Callenberg, Glauchau, Saxony, Germany
4	Hatrurim Formation, Negev, Israel
5	Red Ledge Mine, Washington, Washington District (Omega District), Nevada Co., California, U.S.A.
6	Merume River, Kamakusa, Mazaruni District, Guyana
7	Red Lead Mine, Dundas Mineral Field, Zeehan District, Tasmania, Australia
8	Kaber's Pit, Pokhabikha River Valley, Slyudyanka (Sludyanka), Lake Baikal Area, Irkutskaya Oblast', Prebaikalia (Pribaikal'e), Eastern-Siberian Region, Russia
9	Moon Anchor Mine (Aggravation Mine; East Vulture Mining Co. Mine), Hummingbird Spring, Osborn District, Big Horn Mts, Maricopa Co., Arizona, U.S.A.
10	Potter-Cramer Mine (Potter Cramer Property), Vulture District, Vulture Mts, Maricopa Co., Arizona, U.S.A.
11	Srednyaya Padma Mine, Velikaya Guba Uran-vanadium Deposit, Zaonezhie Peninsula, Lake Onega, Karelia Republic, Northern Region, Russia
12	Akaishi Mine, Doi, Shikokuchuo City, Ehime Prefecture, Shikoku Island, Japan
13	Saranovskii Mine (Saranovskoe), Saranovskaya Village (Sarany), Gornozavodskii Area, Permskaya Oblast', Middle Urals, Urals Region, Russia
14	Zapiga, El Tamarugal Province, Tarapac Region, Chile
15	Unnamed Prospect (Winter Prospect), Eldorado District (Colorado District), Eldorado Mts, Clark Co., Nevada, U.S.A.
16	Chah Khouni Mine (Chah Khoni Mine; Tschah Khuni Mine; El Khun Mine), Anarak District, Nain County (Nayin County), Esfahan Province (Isfahan Province; Aspadana Province), Iran
17	Efim Area, Kumak Ore Field, Orenburgskaya Oblast', Southern Urals, Urals Region, Russia
18	Malyshevskoe Deposit (Mariinskoe), Izumrudnye Kopi Area, Malyshevo, Ekaterinburg (Sverdlovsk), Sverdlovskaya Oblast', Middle Urals, Urals Region, Russia
19	Liu Village, Tongbai Co., Nanyang Prefecture, Henan Province, China
20	MKD5 Nickel Deposit, Mount Keith, Wiluna Shire, Western Australia, Australia
21	Mutnovsky Volcano, Kamchatka Oblast', Far-Eastern Region, Russia
22	Clear Creek Claim (Clear Creek Mine), Picacho Peak, New Idria District, Diablo Range, San Benito Co., California, U.S.A.
23	Bird Nest Drift, Otto Mountain, Baker, San Bernardino Co., California, U.S.A.
24	Garnet Ridge, Dinnehotso, Monument Valley, Navajo Indian Reservation, Apache Co., Arizona, U.S.A.
25	Pipe No. 50, Toudaogou (incl. Pipes No. 51; 68 & 74), Fuxian Kimberlite Field, Wafangdian Co., Dalian Prefecture, Liaodong Peninsula, Liaoning Province (Manchuria; Dongbei Region), China
26	Pit No. 97 (N97 Mine), Ilmen Natural Reserve, Ilmen Mts, Chelyabinsk Oblast', Southern Urals, Urals Region, Russia
27	Ol'khonskiye Vorota Strait (Olkhon Gate), Lake Baikal Area, Irkutskaya Oblast', Prebaikalia (Pribaikal'e), Eastern-Siberian Region, Russia
28	Is River, Isovsky District, Sverdlovskaya Oblast', Middle Urals, Urals Region, Russia
29	Posse Mine (Posse Farm), São José de Brejaúba (São José de Bryamba), Conceição do Mato Dentro, Minas Gerais, Brazil
30	Redington Mine (Boston Mine; Knoxville Mine; Excellsior Mine), Knoxville, Knoxville District, Napa Co., California, U.S.A.
31	Berezovskoe Au Deposit (Berezovsk Mines), Berezovskii (Berezovskii Zavod), Ekaterinburg (Sverdlovsk), Sverdlovskaya Oblast', Middle Urals, Urals Region, Russia
32	Bultfontein Mine, Kimberley, Francis Baard District, Northern Cape Province, South Africa
33	Riland Uranium Claim, Meeker, Rio Blanco Co., Colorado, U.S.A.
34	Orebody 31 (Chromite Deposit 31), Luobusha Mine, Luobusha Ophiolite, Qusum Co. (Qusong Co.), Shannan Prefecture (Lhokha Prefecture; Lhoka Prefecture), Tibet Autonomous Region, China
35	Polar Bear Peninsula (Lake Cowan), Norseman, Dundas Shire, Western Australia, Australia
36	Santa Ana Mine, Caracoles, Sierra Gorda District, Antofagasta Province, Antofagasta Region, Chile
37	Oficina Chacabuco, Sierra Gorda District, Antofagasta Province, Antofagasta Region, Chile
38	Savoleyres, Verbier, Bagnes Valley, Wallis (Valais), Switzerland
39	Weathered Norton County meteorite, Norton Co., Kansas, U.S.A.

Notes: Listed are all localities with at least 4 different Cr mineral species, as well as additional localities that yielded the type specimen for each of the 72 known terrestrial Cr minerals (Table 1a). The identification key to numbers for Cr mineral species appears in Table 1a.

(Table extends on next page)

chromite and magnesiochromite (spinel structure), kosmochlor (pyroxene group), knorringite (garnet group), and eskolaite (hematite structure). Cr minerals discovered exclusively in meteorites are mostly sulfides, phosphides, and nitrides.

Of the 72 essential chemical elements found in at least 1 mineral species (http://rruff.info/ima; Hazen et al. 2015a), 34 are essential constituents of terrestrial Cr minerals. The most frequently encountered elements (Table 3) are oxygen (in 63 species) and hydrogen (33). Next in abundance are common rock-forming elements Mg (17), Si (17), Pb (15), and Ca (11). The remaining 28 elements are each represented by fewer than 10 species. Elements that are not observed in Cr minerals but present in synthetic Cr phases include trace alkali elements such as lithium and transition metals cadmium, molybdenum, and silver (Table 4). The number of essential elements in each Cr mineral range from 1 (the mineral chromium) to 8 [the minerals chromio-pargasite, chromo-alumino-povondraite, polyakovite-(Ce), and vanadio-oxy-chromium-dravite], with most species containing more than three essential elements. Terrestrial Cr minerals are chemically more complex than meteorite species (an average of 4.5 vs. 3.0 essential elements per species), while no significant difference is observed between Cr^{6+} and Cr^{3+} terrestrial minerals (4.5 vs. 4.7 essential elements per species). Compared to meteorite species, proportionally fewer terrestrial species contain S and Fe, whereas proportionally more terrestrial species contain H,

Table 2a. IMA recognized meteorite minerals of chromium, with numbers of recorded occurrences in parentheses (see text), chemical formulas, paragenetic modes, and selected mineral localities (see Table 2b for key to localities, Table 1a for key to paragenetic mode)

No.	Name (No. of Localities)	Formula	Paragenetic mode	Localities
1	Andreyivanovite (3)	FeCrP	9	2
2	Brezinaite (7)	Cr_3S_4	9	3, 4, 5, 7
3	Carlsbergite (25)	CrN	9	1, 3, 6, 7, 14
4	Caswellsilverite (5)	$NaCrS_2$	9	4, 10
5	Chromite (368)	$FeCr_2O_4$	1, 2, 9	1, 2, 3, 5, 6
6	Daubreelite (147)	$FeCr_2S_4$	9	1, 2, 3, 4, 5
7	Eskolaite (8)	Cr_2O_3	3, 9	5, 9, 11, 13, 17
8	Joegoldsteinite (1)	$MnCr_2S_4$	9	20
9	Knorringite (1)	$Mg_3Cr_2(SiO_4)_3$	1, 9	19
10	Kosmochlor (6)	$NaCrSi_2O_6$	1, 9	1, 8, 12, 15
11	Krinovite (2)	$Na_4(Mg_8Cr_4)O_4[Si_{12}O_{36}]$	9	1
12	Magnesiochromite (3)	$MgCr_2O_4$	3, 9	8
13	Murchisite (1)	Cr_5S_6	9	11
14	Schollhornite (4)	$Na_{0.3}CrS_2\ H_2O$	9	2, 4, 10
15	Xieite (1)	$FeCr_2O_4$	9	18

Note: Mineral and locality data were compiled from http://MinDat.org as of April 15, 2016.

TABLE 1b.—*EXTENDED*

No.	No. Cr minerals	Lithological context (key elements)
1	12 (8, 11, 13, 14, 15, 19, 22, 27, 36, 37, 10, 21)	In metaquartzites
2	8 (48, 54, 56, 60, 62, 63, 67, 41)	Au-V-Pb-Zn-Mo-Cu-Ag-W-F (Fluorspar)-Ba (Baryte) mine
3	6 (48, 53, 54, 28, 63, 67)	Oxidized Sb-Cr-As-V-Cu bearing lead deposits
4	5 (4, 45, 57, 35, 39)	Combustion metamorphic rocks
5	5 (8, 20, 22, 32, 36)	Chromite mine in lenses and pods in the serpentine, close to the contact with the sedimentary rocks
6	5 (5, 14, 16, 17, 25)	Placer gravels associated with sandstones, conglomerates and volcanic ash
7	5 (48, 16, 28, 64, 35)	silver lead mine hosted in deeply weathered, dolomite- altered Cambrian ultramafic rocks
8	5 (8, 9, 11, 14, 36)	In metaquartzites
9	4 (48, 58, 63, 67)	Oxidation of Au-Pb-Ag mine hosted in gneiss and schist
10	4 (48, 58, 63, 67)	Oxidation of galena, sphalerite, and pyrite in quartz veins which cut an andesite agglomerate
11	4 (6, 9, 11, 43)	Uranium-vanadium mineralization by near-fault sodium metasomatism and micatization
12	4 (7, 8, 22, 36)	Hosted in serpentine and the neighboring mica schists that were intruded by the serpentine
13	4 (22, 34, 35, 36)	Chromite mine in ultrabasic rocks
14	4 (50, 59, 61, 66)	Deposit with nitrate ore, evaporites
15	4 (54, 58, 60, 63)	Oxidation of Pb-Zn ores in siliceous rocks
16	4 (54, 58, 60, 63)	Oxidation of a low temperature hydrothermal Pb-Zn deposit
17	3 (1, 2, 3)	Hydrothermal Cr-Fe-Au ores
18	3 (8, 14, 24)	In pegmatite
19	3 (2, 22, 71)	Ultramafic to mafic breccias and minor felsic rocks
20	3 (8, 35, 40)	Ni mines in ultramafic complex
21	3 (12, 19, 23)	Mafic volcanic rocks
22	3 (49, 52, 68)	Hg ore in silicified serpentine
23	3 (47, 54, 67)	Pb-U-Te-As-Cr oxysalts
24	2 (8, 22)	Serpentine deposits
25	2 (8, 42)	Diamond mine in a kimberlite pipe
26	2 (8, 29)	Carbonate veins in ultrabasites and amphibolites
27	2 (14, 26)	Metasedimentary rocks
28	2 (70, 71)	Au-Pt bearing placiers
29	2 (46, 51)	In pegmatite
30	2 (8, 31)	Au-bearing mercury mine on the Knoxville Fault at a contact of serpentine, shale, and sandstone
31	2 (44, 8)	Mesothermal gold deposit in quartz veins
32	1 (18)	Diamond mine in a kimberlite pipe
33	1 (33)	On the outer surface and in shallow recesses of a petrified log in sandstone
34	1 (72)	Podiform chromite bodies
35	1 (30)	Oxidation zone of massive nickel sulfides
36	1 (65)	Oxidized zones of lead-bearing deposits in arid regions
37	1 (55)	Oxidized zones of lead-bearing deposits in arid regions
38	1 (38)	No description yet
39	1 (69)	Weathered meteorite

Pb, and other lithophile elements (e.g., K, Ba, Al, V, Si; Tables 1a and 3). This difference can be explained by the fact that Cr, as a lithophile element (Goldschmidt 1937; Bunch and Olsen 1975), is fractionated from siderophile elements, but concentrated together with other lithophile elements during geologic events (e.g., Earth's core-mantle differentiation). Cr minerals formed from these lithophile elements on Earth (e.g., silicates, borates, chromates) tend to contain more essential elements than meteorite Cr minerals (e.g., sulfides), leading to the higher average number of essential elements per species in terrestrial minerals. Within

TABLE 2b. Meteorite names and discovery localities with the greatest diversity of Cr minerals, number and identity of Cr minerals

No.	Locality	No. of Cr minerals
1	Canyon Diablo Meteorite, Meteor Crater And Vicinity, Winslow, Coconino Co., Arizona, U.S.A.	5 (3, 5, 6, 10, 11)
2	Kaidun Meteorite, Hadramawt Governorate, Yemen	4 (1, 5, 6, 14)
3	Sikhote-Alin Meteorite, Paseka Village, Sikhote-Alin Mts, Primorskiy Kray, Far-Eastern Region, Russia	4 (2, 3, 5, 6)
4	Norton County Meteorite, Norton Co., Kansas, U.S.A.	4 (2, 4, 6, 14)
5	Gibeon Meteorite, Gibeon, Mariental District, Hardap Region, Namibia	4 (2, 5, 6, 7)
6	Cape York Meteorite, Saviksoah Peninsula, Qaasuitsup, Greenland	3 (3, 5, 6)
7	New Baltimore Meteorite, New Baltimore, Somerset Co., Pennsylvania, U.S.A.	3 (2, 3, 6)
8	Orgueil meteorite (Montauban; Orgueil), Orgueil, Tarn-et-Garonne, Midi-Pyrénées, France	3 (5, 10, 12)
9	Omolon Meteorite, Magadan, Magadanskaya Oblast', Far-Eastern Region, Russia	3 (5, 6, 7)
10	Yamato 691 Meteorite (Y-691 Meteorite), Queen Fabiola Mts (Yamato Mts), Queen Maud Land (Dronning Maud Land), Eastern Antarctica	3 (4, 6, 14)
11	Murchison Meteorite, Murchison, City Of Greater Shepparton, Victoria, Australia	3 (5, 7, 13)
12	Toluca Meteorite, Jiquipilco (Xiquipilco), Mexico	3 (5, 6, 10)
13	Murray Meteorite, Calloway Co., Kentucky, U.S.A.	3 (5, 6, 7)
14	Yardymly Meteorite, Baku, Yardymli District, Azerbaijan	3 (3, 5, 6)
15	Morasko Meteorite, Poznan, Wielkopolskie, Poland	3 (5, 6, 10)
16	Uegit Meteorite, Dersa, Uegit (Wajid), Bakool Region, Somalia	3 (3, 5, 6)
17	Banten Meteorite, Jawa Barat Province (West Java Province), Jawa Island (Java Island), Indonesia	3 (5, 6, 7)
18	Suizhou Meteorite (Suizhou L6 Chondrite), Xihe, Zengdu District (Cengdou District), Suizhou Prefecture, Hubei Province, China	2 (5, 15)
19	Lewis Cliff 88774 Meteorite (LEW 88774 Meteorite), Lewis Cliff, Buckley Island Quadrangle, Transantarctic Mts, Eastern Antarctica, Antarctica	2 (7, 9)
20	Social Circle Meteorite, Walton Co., Georgia, U.S.A.	1 (8)

Notes: Listed are meteorites with at least 4 different Cr mineral species, as well as additional meteorites that yielded the type specimen for each of the 18 known meteorite Cr minerals (Table 2a). The identification key to numbers for Cr mineral species appears in Table 2a.

Table 3. Coexisting essential elements in chromium minerals, including elements in the 72 terrestrial and 10 meteorite species

Element	Terrestrial total	Terrestrial Cr^{3+}	Terrestrial Cr^{6+}	Meteorites
O	63	37	25	8
H (all with O)	33	20	12	1
Mg	17	15	2	3
Si	17	14	3	2
Pb	15	2	13	
Ca	11	7	3	
S	9	6	2	6
Fe	8	4		4
Na	8	6	2	4
Cu	7	3	4	
C	6	3		
K	6	3	3	
Ti	6	6		
B	5	4	1	
Al	4	4		
Ba	3	2	1	
Cl	3	2	1	
Hg	3		3	
Zn	3	2	1	
Be	2	2		
Bi	2		2	
F	2		2	
I	2		2	
Mn	2	1	1	1
P	2		2	1
V	2	1	1	
As	1		1	
Ce	1	1		
Co	1	1		
Nb	1	1		
Ni	1			
Sb	1	1		
Sr	1	1		
Te	1		1	
N				1

Note: Numbers for these coexisting elements are based on mineral species and chemical formulas in http://rruff.info/ima as of 15 April 2016.

terrestrial minerals, Cr^{6+} species contain more H, Pb, Cu, Hg, F, and Cl, but incorporate common rock-forming elements (e.g., Fe, Mg, Ca, Na, K, B) less often than Cr^{3+} species, in agreement with the observations that most Cr^{6+} species are formed during oxidation of Pb-Cu-Hg deposits at (wet) surface conditions, and that the Cr^{3+} species are mostly rock-forming minerals, including Cr-bearing spinels (chromite), garnets, and tourmalines (Table 1a). Both the rock-forming minerals and the oxidized Pb-Cu-Hg ore minerals can be chemically complex (Table 1a), with similar average numbers of essential elements per species. For both Cr^{6+} and Cr^{3+} terrestrial Cr minerals, association with common anions, including carbonate, phosphate, and vanadate, is very rare (Table 1a). One possible explanation is that, most carbonates, phosphates, and vanadates are either sedimentary or biogenic. Cr is not as intensively involved in bioactivities as other transition metals (Kaim et al. 2013). In addition, Cr^{3+} is very insoluble, while Cr^{6+} is soluble but present as chromate anions in almost all natural fluids (Kotás and Stasicka 2000).

Terrestrial chromium mineral ecology

Hystad et al. (2015) discovered that the distribution of mineral species in Earth's crust conform to a Large Number of Rare Events (LNRE) frequency distribution (Baayen 2001; Evert and Baroni 2008), i.e., a few mineral species occur at many localities, but most minerals are present only at a few localities. This distribution pattern was later reported for carbon, boron, and cobalt minerals (Hazen et al. 2016, 2017; Grew et al. 2016).

Table 4. Estimations of undiscovered species numbers for terrestrial chromium minerals in total and in subsets, calculated from a finite Zipf-Mandelbrot (fZM) model (parameters of the fZM model are listed; see text for discussion)

	All Cr minerals	Cr^{3+}	Cr^{6+}
Alpha	0.7397874	0.7709811	0.6210126
A	0.000122329	0.000152262	0.001247478
B	58.29054	1150.362	1.561854
P-value	0.5030875	0.9018748	0.508251
Current species	72	40	25
Estimated Total	100	53	36
To be discovered	28	13	11
Error	13	10	9
Sample size	4089	3719	347

We modeled the frequency distribution of terrestrial Cr minerals based on the number of known localities for each of the 72 approved terrestrial Cr minerals. The easiest approach to estimating the number of localities for each species is to interrogate the crowd-sourced data resource http://mindat.org, which tabulates locality information for every mineral species. Uncritical use of locality data from mindat.org, however, can lead to errors in the number of localities (Grew et al. 2016; Hazen et al. 2017), which may in turn undermine the frequency distribution model. These errors can be minimized either by checking all available references to verify occurrences of the minerals (Grew et al. 2016), or by removing the geographically redundant mindat.org localities, while adding missing localities cited in the *Handbook of Mineralogy* but not in mindat.org (Hazen et al. 2017). The latter approach was used to examine and update the raw terrestrial Cr-mineral species-locality data from mindat.org.

There are 4089 terrestrial Cr-mineral species-locality data pairs in total, with 24 species recorded at only one locality, an additional 17 species at exactly 2 localities, and 5 species at exactly 3 localities (Table 1). By contrast, more than 70% of these species-locality data relate to one mineral species: chromite (3054 terrestrial localities in mindat.org). The 10 most common Cr minerals account for more than 93% of all species-locality data. This pattern of species distribution among localities, with a few common species and many more rare ones, is typical for the whole set, as well as for various subsets of minerals (Hazen et al. 2015a, 2016; Hystad et al. 2015b; Grew et al. 2016).

The terrestrial Cr-mineral species-locality data are fit to a finite Zipf-Mandelbrot (fZM) model (Hystad et al. 2015a), and the result is summarized in Table 4. The fZM parameters for bulk Cr-mineral species ($\alpha = 0.740$; A = 0.000122; B = 58.3; P-value = 0.503) facilitate modeling of a Cr-mineral accumulation curve (Fig. 1), with a prediction of 100 terrestrial Cr minerals in total. In other words, there are at least 28 Cr minerals on Earth that have not been described. We also applied fZM models to subsets of Cr minerals, including Cr^{3+} and Cr^{6+} minerals (Table 4). The model predicts that there are at least 11 Cr^{3+} minerals and 9 Cr^{6+} minerals to be discovered. Note that parameters A and B correspond to lower and upper cut-off probabilities for the model, and their values should be between 0 and 1. However, B values of the fZM models for all Cr-mineral subsets are much larger than 1 (Table 4), since the sample size (terrestrial species-locality pairs = 4089) is probably not big enough for an accurate LNRE analysis. Nevertheless, these calculations give an approximation of the total/missing Cr minerals, and will become more and more robust as new species-locality data are reported.

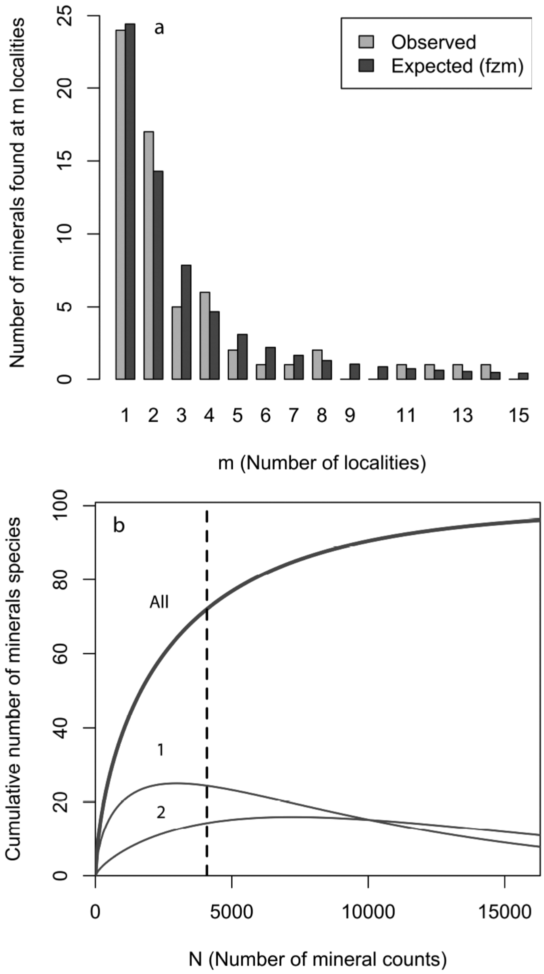

FIGURE 1. (**a**) Frequency spectrum analysis of 72 terrestrial chromium-bearing minerals, with 4089 individual mineral-locality data (from http://mindat.org as of 1 March 2016), a finite Zipf-Mandelbrot (fZM) method to model the number of mineral species for minerals found at exactly 1 to 15 localities (Hystad et al. 2015a). (**b**) This model facilitates the prediction of the mineral species accumulation curve (upper curve, "All"), which plots the number of expected Cr mineral species (*y*-axis) as additional mineral species/locality data (*x*-axis) are discovered. The vertical dashed line indicates data recorded as of 1 March 2016 in mindat.org, as well as locality data from the *Handbook of Mineralogy* (Anthony et al. 2003) and systematic searching under each mineral name in Georef. The model also predicts the varying numbers of mineral species known from exactly one locality (curve 1) or from exactly two localities (curve 2). Note that the number of mineral species from only one locality is now decreasing, whereas the number from two localities is now increasing. We predict that the number of minerals known from two localities will surpass those from one locality when the number of species-locality data exceeds ~10 000.

Errors of the fZM model are estimated in a brute-force Monte Carlo method for bulk terrestrial Cr-mineral species, described as follows. Occurrence probabilities were calculated for each species in the population of 100 terrestrial Cr minerals (including both described and missing species). Based on these probabilities, 500 random samples of size N = 4089 (species-locality pairs) were taken from this population. For each sample fZM LNRE model was refitted and the expected population size S for each sample was calculated. The standard deviation of these population sizes of all 500 random samples was calculated as an error estimation of the fZM model. The result suggests a standard deviation (1σ) of 13 species for total number of terrestrial Cr minerals (i.e., a predicted total of 100 ± 13 species).

IMPLICATIONS: THE "MISSING" MINERALS OF CHROMIUM

The 82 known Cr-mineral species represent only a small fraction of the thousands of known inorganic Cr compounds [Inorganic Crystal Structure Database (http://icsd.fiz-karlsruhe.de)]. Chromium, as all other elements, has the potential to form thousands of mineral species (Hazen et al. 2015b); however, far fewer Cr mineral species would form on Earth because of the special geochemical conditions required to concentrate Cr, similar to other trace elements (Christy 2015; Hazen et al. 2015b, 2017). Here we tabulate 117 synthetic Cr compounds (Table 5) that have not been discovered in nature, but could potentially occur on Earth (or on other highly differentiated planets) as new mineral species.

There are 7 oxides, 11 sulfides, and 7 silicates among the plausible but yet undiscovered Cr minerals (Table 5). Except for the mineral eskolaite (Cr_2O_3), all currently discovered Cr oxides stable at Earth's surface are known only as synthetic phases. Their Cr valences are between +4 and +6, and their crystal structures are diverse (Table 5). Although undiscovered in nature, these synthetic Cr oxides are widely used in industrial processes (Anger et al. 2000). Synthetic stable Cr-bearing sulfides could contain Cr^{2+} or Cr^{3+}. They generally share similar crystal structures to Cr/transition metal sulfide minerals. For instance, a group of synthetic metal Cr sulfides (Table 5) exhibit a chromite-like spinel structure, similar to many metal Cr sulfide minerals (e.g., cuprokalininite, florensovite, kalininite; Tables 1a and 2a). These synthetic Cr sulfides, if present in nature, are more likely to be discovered in meteorites than terrestrial rocks, based on current observations (Tables 1a and 2a).

Synthetic stable Cr silicates possess various crystal structures (Table 5). Both Cr^{2+} and Cr^{3+} can be present, different from Cr silicate minerals currently discovered (Table 1a), which are devoid of Cr^{2+}. The absence of Cr^{2+} can be explained by its complete oxidation in minerals crystallized at mantle oxidation fugacities or higher (Burns 1975). However, recent experimental studies indicate that Cr^{2+} could be dominant in terrestrial (Berry et al. 2006) and planetary (Bell et al. 2014) basaltic melts. Therefore, new Cr^{2+} silicate species can be potentially discovered in the quenched glass of basaltic melts.

Association of Cr with other common anions (e.g., carbonates, phosphates, vanadates) is rare not only in natural minerals (Table 1a), but also in synthetic compounds. The scarcity of synthetic compounds that contain these additional anions implies that the chance of finding new Cr carbonate, phosphate, or vanadate minerals is very small.

Chromates are dominant (82 species) in the list of synthetic Cr compounds that are plausible but as yet undiscovered Cr minerals (Table 5). A few of these synthetic compounds share similar structures to known Cr minerals (e.g., lopezite, crocoite, heshemite). However, the majority of them possess different crystal structures. Chemical compositions of these synthetic

TABLE 5. Plausible as yet undescribed primary chromium minerals, based on synthetic Cr-bearing phases tabulated in the International Crystal Structure Database (http://icsd.fiz-karlsruhe.de)

Formula	Structure type	Related known minerals
	Oxides	
CrO_2	rutile	
CrO_2	pyrite	
CrO_2	$CaCl_2$	
CrO_3		
Cr_5O_{12}	$Al_2(WO_4)_3$	
Cr_3O_8		
Cr_8O_{21}		
	Sulfides	
$CdCr_2S_4$	spinel	
$CoCr_2S_4$	spinel	
$NiCr_2S_4$	spinel	
$HgCr_2S_4$	spinel	
$KCrS_2$	caswellsilverite	
$LiCrS_2$	caswellsilverite	
CrS	nickeline-NiAs	
$BaCrS_2$		
Cr_2S_3		
Cr_5S_8		
$CrMo_2S_4$		
	Silicates	
$Ca(CrSi_4O_{10})$	gillespite	
$Ca_2Al_{1.5}B_{0.5}Si_{0.5}Cr_{0.5}O_7$	melilite	
Cr_2SiO_4	Na_2SO_4	
$Cr_4Na_{44}(AlO_2)_{56}(SiO_2)_{136}\cdot(H_2O)_{245}$	faujasite	
$Cr_4Br_2Si_2O_7$		
$Cr_4Cl_2Si_2O_7$		
$[Cr_3(Si_2O_7)](NaCl)_{0.25}$		
	Sulfates	
$Cr_2(SO_4)_3$	millosevichite	
$KCr_3(SO_4)_2(OH)_6$	alunite	
$KCr(SO_4)_2$	steklite	
$LiMgCr_3(SO_4)_6$		
$KCr(SO_4)_2\cdot(H_2O)_{12}$		
$NaCr(SO_4)_2\cdot(H_2O)_{12}$		
$[(CH_3)NH_3]Cr(SO_4)_2\cdot(H_2O)_{12}$		
	Chromates	
$K_2(CrSO_7)$	lopezite	
$SrCrO_4$	monazite	
$HgCrO_4$	monazite	
$K_2Mg(CrO_4)_2\cdot(H_2O)_2$	fairfieldite	
$Mg(CrO_4)$	$CrVO_4$	lopezite
$Mg(CrO_4)$	$CoMoO_4$	hashemite, crocoite
$CdCrO_4$	$CoMoO_4$	
$CoCrO_4$	$CoMoO_4$	
$CuCrO_4$	$CoMoO_4$	
$MnCrO_4$	$CoMoO_4$	
$NiCrO_4$	$CoMoO_4$	
$CaCrO_4$	zircon	
Ag_2CrO_4	olivine	
$K_2(CrO_4)$	K_2SO_4	
$(NH_4)_2CrO_4$	K_2SO_4	
$KLi(CrO_4)$	K_2SO_4	
$Li_2(CrO_4)$	K_2SO_4	
$Na_2(CrO_4)$	K_2SO_4	
$Ca_8(AlO_2)_{12}(CrO_4)_2$	aluminate sodalite	
$[Mg(H_2O)_4](CrO_4)\cdot(H_2O)$		
$(NH_4)Fe(CrO_4)_2$		
$(NH_4)_2[Cd(NH_3)_2(CrO_4)_2]$		
$(NH_4)_2[Cu(CrO_4)_2(NH_3)_2]$		
$(NH_4)_2[Ni(H_2O)_6](CrO_4)_2$		
$(NH_4)_2Zn(NH_3)_2(CrO_4)_2$		
$(CH_3)_4N)[C(NH_2)_3]CrO_4$		
$[Co(NH_3)_6](CrO_4)Cl\cdot(H_2O)_3$		
$(H_3O)_6[UO_2(CrO_4)_4]$		
$(Pb_3O)_2(BO_3)_2(CrO_4)$		
$(UO_2)(CrO_4)\cdot(H_2O)_x$		
$Al_2(CrO_4)_2Cr_2O_7\cdot(H_2O)_4$		
$Bi[CrO_4(OH)]$		
$Bi_8(CrO_4)O_{11}$		
$CaCrO_4\cdot(H_2O)$		
$Ca_2[(UO_2)_3(CrO_4)_5]\cdot(H_2O)_{19}$		
$CuPb_{10}(CrO_4)_6(SiO_4)_2(OH)_2$		
$Cu_2CrO_4(OH)_2$		
$Fe_2(CrO_4)_2(Cr_2O_7)\cdot(H_2O)_4$		
$Fe_2(CrO_4)_3\cdot(H_2O)_3$		
$Hg(CrO_4)\cdot(H_2O)$		
$Hg(CrO_4)\cdot(H_2O)_{0.5}$		
$K(UO_2)(CrO_4)(NO_3)$		
$K[UO_2(CrO_4)F]\cdot(H_2O)_{1.5}$		
$K(UO_2)(OH)(CrO_4)\cdot(H_2O)_{1.5}$		
$KAl(CrO_4)_2\cdot(H_2O)_2$		
$KBi(CrO_4)(Cr_2O_7)\cdot(H_2O)$		
$KCr(CrO_4)_2$		
$KFe(CrO_4)_2$		
$KFe(CrO_4)_2\cdot(H_2O)_2$		
$KFe(CrO_4)_2\cdot H_2O$		
$KFe_3(OH)_6(CrO_4)_2$		
$KMn_2(CrO_4)_2(OH)\cdot(H_2O)$		
$K_2[(UO_2)_2(CrO_4)_3(H_2O)_2]\cdot(H_2O)_4$		
$K_2[UO_2(CrO_4)(IO_3)_2]$		
$K_2Ba(CrO_4)_2$		
$K_3MnO_4CrO_4$		
$K_3Na(CrO_4)_2$		
$K_4[(UO_2)_3(CrO_4)_5]\cdot(H_2O)_8$		
$K_4(CrO_4)(NO_3)_2$		
$K_5[(UO_2)(CrO_4)_3](NO_3)\cdot(H_2O)_3$		
$K_6[(UO_2)_4(CrO_4)_7]\cdot(H_2O)_6$		
$K_8[(UO_2)(CrO_4)_4](NO_3)_2$		
$La(OH)(CrO_4)$		
$Li_2(CrO_4)\cdot(H_2O)_2$		
$Mg(CrO_4)\cdot(H_2O)_{11}$		
$Mg(CrO_4)\cdot(H_2O)_5$		
$Mg_2[(UO_2)_3(CrO_4)_5]\cdot(H_2O)_{17}$		
$NH_4Cr(CrO_4)_2$		
$NH_4Fe(CrO_4)_2$		
$Na(NH_4)(CrO_4)\cdot(H_2O)_2$		
$NaAl(CrO_4)_2\cdot(H_2O)_2$		
$NaCr(CrO_4)_2$		
$NaFe(CrO_4)_2\cdot(H_2O)_2$		
$Na_2CrO_4\cdot(H_2O)_4$		
$Na_4[(UO_2)(CrO_4)_3]$		
$Pb_2(HgO_2)(CrO_4)$		
$Pb_2(Hg_3O_4)(CrO_4)$		
$Pb_2Mn_2O_5(CrO_4)$		
$Pb_4(PO_4)_2(CrO_4)$		
$Pb_5O_4(CrO_4)$		
$REE_2(CrO_4)_3\cdot(H_2O)_x$		
$Sr(UO_2(OH)CrO_4)_2\cdot(H_2O)_8$		
	Other anions	
$Cr_2(CO_3)_3$		
$CrPO_4$		
$CrPO_4\cdot(H_2O)_x$		

chromates are very diverse, containing most lithophile, chalcophile, and some siderophile elements as essential elements. Based on their chemistry (Table 5b) and the paragenetic modes of current chromate minerals (Table 1a), we propose that the synthetic chromates may be discovered in (1) a very highly oxidized environment, indicated by the chromate anion and other oxidized cations (e.g., U^{6+}, Fe^{3+}); (2) a very arid environment for the highly soluble species [e.g., Na_2CrO_4, $K_3Na(CrO_4)_2$]; or (3) an oxidized ore deposit for the Pb-Ag-Cu-Hg species.

A few Cr sulfates are also listed in Table 5. Only three Cr sulfate minerals have been discovered in nature (Table 1a), and none are related to the synthetic species. Thus it is difficult to infer their possible occurrences. It can be only speculated that if these compounds are present in nature, they may form during weathering processes, similar to aluminum sulfates (e.g., potassium alum; millosevichite), due to their crystal-structure similarity. Several species containing $[CrO_4]^{3-}$ or $[CrO_4]^{4-}$ have also been successfully synthesized (e.g., Delnick et al. 1985), however, they are not included in Table 5 because they are extremely unstable and undergo rapid disproportionation to Cr^{3+} and Cr^{6+} in aqueous fluids (e.g., Krumpolc and Rocek 1976).

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