Revision 1

# How many boron minerals occur in Earth's upper crust?

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## ABSTRACT

The current rate of discovery of new boron minerals (65 species or potential species described from 2008 to 2017) is higher than at any prior 10-year period, implying that rates of B mineral discovery could increase further with no obvious limit to boron mineral diversity in Earth's crust. In contrast, large number of rare events (LNRE) models calculated from the 295 species of B minerals discovered through 2017 give a total predicted B mineral endowment in Earth's crust of 459 ± 65.5 and 523 species, using a finite Zipf-Mandelbrot (fZM) model and Sichel's generalized inverse Gauss-Poisson model (GIGP), respectively, i.e., there is a very real predicted limit of no more than ~500 species. As cautioned by Hazen, Hystad and their co-authors, LNRE modeling presumes no changes in how minerals are discovered from the beginning of mineral discoveries in the late 18th century to early 2017. However this condition is clearly not the case, and thus changes could explain the discrepant indications. The most important changes are: (1) the advent of the electron microprobe, which became widely used for chemical analysis of B minerals in 1978; (2) technological advances in single-crystal X-ray diffractrometry, (3) technological advances in electron microscopy including advent of electron backscattered diffraction; (4) advent of micro-Raman spectroscopy; and (5) changes in mineralogical nomenclatures, particularly of the tourmaline supergroup. Changes (1) to (4) are expected to reduce the size of the mineral grains that can be studied, thereby increasing the number of species accessible to study. Furthermore, should species have a fractal distribution (i.e., diversity is independent of scale) examination of increasingly smaller grains will turn up an even larger number of species. In order to evaluate the impact of these changes on the LNRE modeling, we modeled the 146 B minerals discovered up through 1978, which was selected as the cutoff because of (1) the important role played subsequently by the electron microprobe and (2) the number of species was 50% of the current number. This modeling gave 306 (fZM) and 359 (GIGP) for total species, i.e., the access to smaller grains afforded by advanced analytical instrumentation has resulted in an increased estimate of total endowment by 50% from 1978, whether the fZM or GIGP distribution is applied. We doubt that the ~500 B species estimate is the end of the story, as we expect there will be further technological advances in the future. A more realistic finale might come when we reach the natural limit imposed by the minimum number of unit cells needed for new mineral to be viable, and thus LNRE modeling might yet show that Earth's total endowment of B minerals is finite.

A review of past patterns of discovery of new boron minerals, which can inform us what to expect in future discoveries, reveal that only 19% of B minerals were synthesized prior to discovery. We conclude that synthetic compounds are not a particularly promising source of potential new B minerals. In contrast, 22% B minerals were discovered prior to synthesis and 29% have unique structures, i.e., they have no synthetic analogues and are not isostructural with a known mineral. Accordingly, 41% of B minerals could not be predicted, and we conclude that the realm of as yet undiscovered B minerals holds a significant number of surprises.

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## INTRODUCTION

Measuring the total number of species, whether plant, animal, or mineral, has been a matter of interest and discussion for well over a half century. Since the pioneering studies of Fisher et al. (1943) relating the number of species and number of individuals in a given area, biologists have attempted to estimate species diversity in a given area from a limited sampling (e.g., Miller and Wiegert 1989, Shen et al. 2003; Bunge et al. 2014; Hystad et al. 2015a and references cited therein). Mineralogists have also discussed similar questions relative to Earth's mineral endowment. Among the first was A.E. Fersman (1938), who sought an explanation for the relative paucity in the mineral kingdom – his estimate was about 3000 species. Povarennykh (1966) discussed constraints on number of species, numbering 1660 by his count, imposed by crystal chemical properties. Urusov (1983) provided a firmer theoretical foundation for this relatively low diversity, by his estimate not to exceed 2500, and he predicted there would come a time when no new mineral discoveries would be made. However, new mineral discoveries accelerated (Fig. 1), which led Khomyakov (1994, 1996) to challenge these pessimistic assessments by contending that geological entities with extraordinary mineralogical diversity, notably the agpaitic Khibiny and Lovozero complexes on the Kola Peninsula, were greatly increasing overall mineralogical diversity. Bulakh et al. (2001, 2012) parsed the reasons for the surge in new mineral discoveries by considering the roles played by the electron microprobe, crystal structure refinement, and nationality.

Little cognizant of work published in the Russian-language literature, Hazen et al. (2015a,b) and Hystad et al. (2015a,b) addressed similar questions as the Russian mineralogists, but used a different approach, which is based on the Large Number of Rare Events (LNRE) model. The LNRE model, which finds wide use in calculating an author's vocabulary from word frequencies in the author's text (Baayen 2001), can be applied to calculate how many mineral species there could be in Earth's crust from the number of species already discovered. For example, the number of minerals remaining to be discovered, or "missing minerals", was estimated to be 1563 compared to 4831 already discovered as of 2014 (Hazen et al. 2015a,b) assuming the methods used to find and characterize new minerals remained the same, as would the sizes of the mineral grains under study. However, these methods have changed drastically over the last 50 years, as has the scale at which minerals were studied, vastly accelerating the rate of discovery, such that at the present rate of new mineral approvals (Figure 1), the 1563 minerals could all be found in 15-20 years. The end of new mineral discoveries in such a short time seems as improbable to us now as Usurov's (1983) prediction must have appeared to some mineralogists 30 years ago.

Hazen et al. (2015a) also introduced the hypothesis of "total potential mineral diversity", calculated to be 15,300 species assuming each of the 72 essential mineral-forming elements is represented by 1000 potential minerals containing on the average 4.7 essential elements (cf. Khomyakov 1994, who used a simpler calculation to estimate the number of potential minerals in peralkaline complexes). Clearly such diversity could be attained only over a very large compositional space, most plausibly encompassing a large number of extrasolar planets, in which even the rarest of elements are locally abundant, such as beryllium on the fictional extra-solar planet Junior in *Sucker Bait* (Asimov 1954).

Our objective in the present paper is to reconcile the contradictory predictions from the LNRE model and current rate of new mineral discoveries using boron minerals as an example. With only 296 species, including approved and potentially valid (as of early 2017), the subset of B minerals is manageable, allowing for consultation of primary literature in a reasonable amount of time; much of the necessary information is not available in the crowd-sourced mindat.org or compendia such as the *Handbook of Mineralogy* (Anthony et al. 1990-2003). First we aim to review factors that could impact LNRE models such as definition of a locality, sample size of type material, and the advent of more advanced technology in the characterization of new boron minerals. For evaluating the impact of technology, we have chosen the advent of the electron microprobe because its use for boron minerals increased markedly in 1978 only 4 years after first use (Fig. 2), despite the difficulty in analyzing B with this instrument and the susceptibility of boron minerals to breakdown under the electron beam. In contrast improvements in single-crystal X-ray diffraction methodology were more incremental and introduction of other methods such as micro-Raman spectroscopy were less pervasive. We will show that the electron microprobe did accelerate the rate of discovery of boron minerals as Hazen et al. (2015a,b) and Hystad et al. (2015a,b) had suspected, resulting in a larger number of “missing” minerals. The increasingly smaller grains that can be studied with the electron microprobe, electron microscope, and other microbeam instruments (Fig. 3) could greatly expand the number of minerals discovered, particularly if diversity is fractal ( i.e., independent of scale). Secondly, we consider the potential of synthetic compounds to predict the identities of as yet undiscovered minerals, as revealed in the history of new mineral discoveries and synthesis of analogues. We find that the potential predictive power of synthetic compounds is less than one might expect. More than half of new B minerals are compounds that either have never been synthesized or had not been synthesized at the time the mineral was discovered.

## DEFINITIONS AND CRITERIA USED IN COMPILING THE DATABASE

### Mineral species

Tables 1 and 2 (Appendix 1; bibliography Appendix 2) lists in alphabetical order the 296 minerals (of which 295 were include in the LNRE models) containing essential B including (1) 278 of the 280 species considered valid (as of February, 2017) by the Commission on New

Minerals, Nomenclature and Classification of the International Mineralogical Association (CNMNC IMA) together with their formulae and date of discovery, which were taken from the 2017 CNMNC IMA list (the list can be downloaded from the CNMNC IMA website or the RRUFF website, http://rruff.info/ima/), together the most recent CNMNC Newsletters. Group assignment is based largely on Back (2014) and Mills et al. (2009). We have chosen the CNMNC IMA list as the basis for deciding what constitutes a mineral species primarily because this list is widely recognized and accepted in the mineralogical community.

Nonetheless, our list does differ from the 2017 CNMNC IMA list in that three species in that list are not included in ours, and 17 potential species have been added. We follow Grew et al. (2016) in excluding ericaite, and melanocerite-(Ce). In addition, we have taken calcybeborosilite-(Y) off both our 1978 and 2017 lists because it is given as “questionable” in the list at the CNMNC IMA website and because it is believed to represent an intermediate composition between hingganite-(Y) and datolite (Cámara et al. 2008).

Added species include 8 tourmaline species; $B_4C$; $TiB_2$; “Mg-blatterite”; three unnamed borates two of which contain ammonium; Walenta’s (1976, 2008) unnamed uranium mineral B; a monoclinic analogue of malinkoite, $NaBSiO_4$; a Th borosilicate, and a $CO_3$-rich charlesite (last not included in LNRE modeling). In contrast, Walenta’s (1976) unnamed uranium minerals A and C or the hexagonal modification $NaBSiO_4$; reported as UK53B from Mont Saint-Hilaire (Wight and Chao 1995) do not seem sufficiently well characterized to be considered potential new minerals at the present time. We no longer consider “tadzhikite-(Y)” a potential species (Table 3, Appendix 3).

“Bakerite” was discredited in 2016 (IMA 16-A, Hålenius et al. 2016; Bačík et al. in press), and thus not included in the 2017 list; “bakerite” was also removed from the 1978 list, although it was considered valid at that time.

The date of discovery is the year when a full description of the species was published, or, at least, a partial description in an abstract. Publication of the mineral in the CNMNC lists and Newsletters is not counted as the year of discovery unless this is the only information on a mineral, as is the case of some minerals discovered in the last year or so. Publication in the lists and Newsletters generally precedes full description by a year or two, rarely more.

## Synthetic analogues of minerals

In principle, synthetic analogues (Table 2, Appendix 1, with bibliography in Appendix 2) should be easily recognized by having the same composition and crystal structure as the mineral, but in practice this comparison is not so simple. Reports of syntheses in the older literature do not always provide sufficient data to conclusively confirm an analogue. Difficulties can arise when several polymorphs of a compound have been synthesized, e.g. parasibirskite and sibirskite (Sun et al. 2011), and often not all have been found naturally, e.g. frolovite (Fleischer 1958; Zeigan 1966; Simonov et al. 1976a) and suanite (Guo et al. 1995). Despite the many syntheses of compounds related to hilgardite, none are analogues of known minerals as they differ slightly in composition and structure, although in one case, the structures are the same, but a small difference in composition still precludes equating the mineral and the corresponding synthetic: leucostaurite, $Pb_2[B_5O_9]Cl\cdot 0.5H_2O$, space group *Pnn*2 versus synthetic $Pb_2[B_5O_9]Cl$, also space group *Pnn*2 (Brugger et al. 2012).

The tourmaline supergroup illustrates the difficulty of synthesizing compositionally complex natural compounds and confirming that the synthetics are valid analogues, although synthetic and natural tourmalines are isostructural. Of the 40 currently recognized and potential species in the tourmaline supergroup, synthesis of only 7 can be considered confirmed (Table 2, Appendix 1), four in the $Na_2O$-$MgO$-$Al_2O_3$-$SiO_2$-$B_2O_3$-$H_2O$ system plus schorl (e.g., van Goerne et al. 1999; London 2011), “oxy-magnesio-foitite” (von Goerne and Franz 2000), and rossmanite (reported as elbaite-dominant, Guttery 2012; “Li-rich tourmaline”, Kutzschbach et al. 2016). Most tourmaline species contain essential FeO, $Fe_2O_3$, $Li_2O$, or F, and a fair number, either $Cr_2O_3$ or $V_2O_3$ or both. Even in the relatively simple system, subtle compositional differences exist between synthetic and natural tourmalines. The only tourmaline synthesized by von Goerne and Franz (2000) in the $CaO$-$MgO$-$Al_2O_3$-$SiO_2$-$B_2O_3$-$H_2O$ system was “oxy-uvite”, whereas the only natural tourmaline in this system is uvite (Henry et al. 2011). Similarly, for the $K_2O$-$MgO$-$Al_2O_3$-$SiO_2$-$B_2O_3$-$H_2O$ system, Berryman et al. (2014) synthesized the K-analogue of dravite, whereas the only natural tourmaline is maruyamaite, the K-analogue of oxy-dravite (Lussier et al. 2016).

## Localities – a critical component in LNRE models

In applying LNRE models, a linguist’s tool, to mineral diversity Hazen et al. (2015a,b) and Hystad et al. (2015a,b) equated mineral species diversity with vocabulary and mineral species/locality pair with word count. The total mineral species/locality pairs are equal to the sum of minerals reported from 1 locality + twice the number of minerals reported from 2 localities + thrice the number of minerals reported from 3 localities, and so forth. The main difficulty in counting an exact number of discrete mineral localities for each mineral species is that what constitutes a species and what constitutes a locality are less precisely defined than what constitutes a word in a document. We think that adoption of the CMNMC IMA definition of a species should minimize problems in regard to species (see above), but the definition of what constitutes a locality has turned out to be far more difficult.

Table 3 (Appendix 3; bibliography Appendix 4), together with the supplement accompanying Grew et al. (2016), list localities for boron minerals occurring at 20 localities or less, plus a few occurring at more than 20 localities; the remaining localities were taken from the crowd-sourced database at http://www.mindat.org with the assistance of Joshua Golden.. Grew et al. (2016) adopted a more stringent definition of a locality than used at http://www.mindat.org. Examples of what mindat.org lists as multiple localities, but what which we consider to be single localities are (1) pegmatites associated with Larvik plutonic complex in the Langesundsfjord area south of Oslo, Norway (Larsen 2010); (2) pegmatites associated with the Ilímaussaq complex in southwest Greenland; (3) Långban-type deposits near Filipstad, Sweden; (4) Sterling Hill, Franklin Furnace, and other mines in the Franklin Marble in the vicinity of Ogdensburg, Franklin and Hamburg, Sussex County, New Jersey, (5) the Chicagon and Bengal mines east of Iron River, Iron County, Michigan (Heinrich and Robinson 2004); (6) Vielle-Aure, Tuc de Boup and Jurvielle, Hautes Pyrénées, France; and (7) borate deposits in the Furnace Creek formation, Death Valley, California. Each of these localities comprises a fair number of individual occurrences that we do not recognize as distinct localities because they are closely spaced and have identical ages. However, other cases have proved to be more of a challenge to decide on whether localities are distinct, for example, evaporite deposits. We now consider borate-bearing strata in the Penobsquis and Millstream deposits near Sussex, New Brunswick as distinct (cf. Grew et al. 2016) because each was deposited in separate troughs having different depositional environments (Grice et al. 2005). Other evaporite deposits posing similar problems are the Zechstein of Europe: Yorkshire, UK (Kemp et al. 2016) and Saxony-Anhalt, Germany (e.g., Kühn 1972; Heide et al. 1980); in these areas, we have generally accepted different localities as distinct. Another case is the Eifel region in Germany, where occurrences are associated with different volcanic edifices, and should be considered distinct localities although similar in age.

Another problem is inadequate characterization of localities. The provenance of specimens from Madagascar is not always adequately specified. Reports of specimens from China and the former Soviet Union dating from the 1950s, 1960s and early 1970s  include only vague indications of localities (e.g., "eastern Siberia", "Far East"), if any at all; in some cases locality information can be obtained from later publications (e.g., Pekov 1998). Applying this standard required consultation of the primary literature. Because such consultation was practical only for B minerals found at no more than about 20 localities worldwide, whereas mindat.org was used for the most widespread minerals, e.g., datolite, elbaite, and schorl as of January 15, 2016.

There are a few reports that we decided were not sufficiently well substantiated to justify inclusion in the locality list: (1) sakhaite, sulfoborite and others reported by Semeykina and Kozlova (1984, 1985), who were cited by Mazurov et al. (2007) and (2) brianroustanite, hydrochloroborite and others reported by Koçak and Koç (2016).

The problem of determining the exact number of localities for each mineral species became more acute for the minerals discovered in 1978 or earlier—data that we needed to assess the impact of the electron microprobe (see below). Some minerals were recognized as distinct before 1978 but could not be fully characterized until afterwards, e.g., iquiqueite (Ericksen et al. 1986), and consequently, was not included in the 1978 list; the problems raised by solid solutions and polytypism are considered in a separate section.

For the minerals reported from more than 20 localities prior to 1979—too many localities to examine every primary source—we used mineral species/locality pairs from mindat.org multiplied by 50.1% (Table 1, Appendix 1), the ratio of mineral-locality counts that could be checked from primary sources in 1978 (398) versus 2017 (795 out of the 1124 total counted). It was not possible to "unwind" the mindat.org database to get locality counts for 1978 directly as compilation of the database commenced in 1991. The total mineral species/locality pairs for 1978 are 3214, somewhat less than half of the 7024 mineral species/locality pairs for 2017.

Admittedly, these totals are approximations. However, Hazen et al. (2015b) argued that when such large numbers of localities are involved, database errors, such as how localities are defined, omissions, and misidentified minerals, will not introduce significant bias if used for discerning large-scale patterns [following Adrain and Westrop (2000), who justified use of a comparable global database of fossil genera "rife" with error)].

In the final analysis, the more stringent locality definition for minerals with up to 20 localities had a significant impact on the calculated LNRE model, as it gave a greater proportion of "missing" minerals than using mindat.org data exclusively (i.e., Hazen et al. 2015b) reported 26.1% "missing" of 265 B minerals using exclusively the crowd sourced data, whereas we obtained 35.7% missing of 295 B minerals, in both cases using the finite Zipf–Mandelbrot model (see below).

### Solid solutions and polytypism

The localities for solid solutions other than tourmaline-group minerals, that is, hulsite-magnesiohulsite, warwickite-yuanfuliite, fluoborite-hydroxylborite, and kornerupine-prismatine, are undercounted since reports without compositional data or reliable proxies for composition cannot be counted. Further difficulties, arose if one end member were discovered prior to 1978 and the other afterwards. For hulsite-magnesiohulsite, compositions recognized as Mg-dominant before the formal description of magnesiohulsite in 1985 were nonetheless included as magnesiohulsite in the 1978 list. The solid solution series fluoborite-hydroxylborite and rhodizite-londonite are special cases in that type fluoborite is actually hydroxylborite (Rudnev et al. 2007) and type rhodizite is actually londonite (Pekov et al. 2010). We concluded that the best approach to these anomalous situations was to move up the discovery dates of hydroxylborite and londonite to 1926 and 1834, respectively, and considered the date of discovery of the other two end members to be better defined by the confirmation of an F-dominant analog of fluoborite ("nocerite", Brisi and Eitel 1957; Flamini 1966) and of a K-dominant analog of londonite (Pring et al. 1986), respectively. The distinction between kornerupine (B < 0.5 atoms per formula unit) and prismatine (B > 0.5 apfu) became possible only after Moore and Araki (1979) had identified a unique crystallographic site for boron in the structure (Grew et al. 1996). Thus, counts for the kornerupine-prismatine series in the 1978 list are based on the total number of localities reported for kornerupine irrespective of boron content, whereas counts in the 2017 list require knowledge of the B content so that kornerupine and prismatine could be distinguished. An analogous approach was adopted for warwickite-yuanfuluite: there are several reports of warwickite unaccompanied by a chemical analysis that can be considered valid before yuanfuliite was discovered, but became invalid when yuanfuliite was recognized as a distinct species

Uvite and fluor-uvite constitute yet another special case. In contrast to the minerals described above, there are too many localities reported at http://www.mindat.org for uvite (140) and fluor-uvite (19) to check each individually for F content, which is needed to distinguish these two tourmaline species. Since the distinction between uvite, feruvite, and fluor-uvite was not recognized before 1978 (e.g., Dunn et al. 1977; Hawthorne and Henry 1999), we have counted the localities for an uvite sensu lato that includes all Ca-dominant compositions irrespective of Mg/Fe and F/OH ratios in the 1978 list (Appendix 3). This locality count is undoubtedly incomplete although we consulted several compilations (Dunn et al. 1977; Chukhrov 1981; Deer et al. 1986) as well as http://www.mindat.org. Unfortunately, several reports listed in http://www.mindat.org could not be confirmed upon consultation of the original, and thus verification of all the reports in http://www.mindat.org was not attempted. Use of the total counts in http://www.mindat.org for the 2017 list is also problematic. It is unlikely that uvite is over 7 times more abundant than fluor-uvite: The Ca vs. F plot for over 8000 tourmaline compositions (Henry et al. 2011, Fig. 2b) show  that tourmaline with Ca > 0.5 (liddicoatite and uvite) tend to be F > dominant. For simplicity, we simply split the difference for 2017: 80 mineral species/locality pairs for fluor-uvite and 79 mineral species/locality pairs for uvite. We expect the impact of this decision on the modeling to be negligible..

Discovery that supposed polymorphs are polytypes results in the reverse situation: a decrease in the number of species. Two polymorphs of veatchite were recognized prior to 1978 (and a third in 1979) and were treated as polymorphs (distinct species) by Grice et al. (1999), whereas Grice and Pring (2012) treated them as polytypes of a single species. Thus there are two entries for veatchite in the 1978 list, but one entry in the 2017 list (Table 3, Appendix 3). It does not appear that a similar fate will befall kurchatovite and clinokurchatovite, although Belokoneva (2003) concluded that these minerals are polytypes. Our own investigation (Pankova, Krivovichev, Grew, Pekov, in preparation) support the conclusion by Callegari et al. (2003) that the two minerals are distinct species. Moreover, since both were reported prior to 1978, they are included in the 1978 list, although the formal description of clinokurchatovite was published in 1983.

For the compilation of grain sizes at the time of discovery, the original mineral names are retained (Table 2, Appendix 1).

## DISCOVERY OF BORON MINERALS: PAST, PRESENT, AND FUTURE

The number of B minerals discovered in any one 10-year interval shows a steady increase throughout the 19th and 20th centuries and continuing into the 21st century; major exceptions being a dip a few years after World War I and a spike in the early 1960s (Figs. 4, 5). The latter results from the large number of borates discovered between 1957 and 1966 in evaporite and skarn deposits in the former Soviet Union at that time.

Since about 1865, the number of boron minerals having synthetic analogues remained relatively constant except for a spike in the early 1960s. Up until the mid-1920s, nearly all new boron minerals had either been synthesized or would eventually be synthesized, although in some instances only after a long interval, e.g., 103 years for dumortierite (Werding and Schreyer 1984, 1990). The proportion of minerals synthesized prior to discovery in nature increases with time and, after 1970, surpasses the proportion of minerals synthesized after discovery, a situation that could change with syntheses in the future. Overall, 120 B minerals, 41% of the 296 total, have synthetic analogues, consistent with Khomyakov's (1994) inference that only one half of all minerals would have synthetic analogues. Conversely, as Khomyakov (1994) noted for all minerals and synthetics, it is likely that the number of synthetic boron compounds having natural analogues is a small fraction of the total number of synthetic boron compounds; e.g., in their review of over 100 alkali and alkaline borates, Touboul et al. (2003) mentioned only 10 minerals by name. However, there are exceptions in a few subsets of boron minerals, e.g., tourmaline supergroup (see above) and the axinite group (only one synthetic analogue of 4 minerals, Table 2, Appendix 1). The motivation to synthesize boron minerals has largely been twofold: (1) to understand the physico-chemical conditions under which the minerals formed, for example Ca, Mg, and other borates (Meyerhoffer and van't Hoff 1907; Nekrasov et al. 1970; Nekrasov 1973) and both borates and borosilicates by Werner Schreyer, Günter Werding, and their colleagues and students (e.g., Werding and Schreyer 1996); and (2) industrial applications other than as an ore of B compounds, e.g., compounds isostructural with peprossiite-(Ce) in laser technology (Capitelli et al. 2009, 2011) and compounds isostructural with pinakiolite as catalysts (Bovin and Norrestam 1990). Not all syntheses are targeted; some are serendipitous, such as jeremejevite (Michel-Lévy 1949) and pseudosinhalite (Werding and Schreyer 1996).

After 1960, compounds that are either isostructural with existing minerals or unique, having no natural or synthetic analogues, increased, particularly in the last 10 to 20 years, leading to the rapid surge of new B minerals since 1990. A major contribution to this surge is from new species in the tourmaline supergroup, undoubtedly spurred by publication of the new tourmaline nomenclature (Henry et al. 2011).

How do the past patterns of discovery inform us what to expect in future discoveries? Grew and Hazen (2014) suggested that new Be minerals could be: (1) analogs of known minerals, particularly if the analogs had already been synthesized, and (2) one of the many known synthetic compounds. Hazen et al. (2016) identified 432 plausible carbon minerals not yet discovered that would include 242 natural analogues of known synthetic compounds and 190 isostructural with known carbon minerals. Of the 296 B minerals listed in Table 1 (Appendix 1), 146 or 49% are either isostructural or form a solid solution series with at least one other mineral (not always a B mineral), thus providing a historical justification for searching for potential new minerals by considering possible isostructural analogues of known minerals, e.g., a new tourmaline supergroup or ludwigite-group mineral. Nonetheless, discoveries of boron minerals suggest a somewhat different pattern. Taking as an example the 31 ternary compounds in the $CaO$-$B_2O_3$-$H_2O$ system for which the crystal structures are known (Table 4), we find 21 of the 22 known minerals in this system, but only 23 of potential synthetics. For instance, Nekrasov et al. (1970) and Nekrasov (1973) listed an additional 3 synthetics in this system: $CaB_4O_7 \cdot 2H_2O$, $Ca_2B_{10}O_{17} \cdot 3H_2O$, and $Ca_2B_{10}O_{17} \cdot 5H_2O$. Seven of the listed minerals have no known synthetic analogue, 8 minerals were discovered prior to synthesis, and 6 minerals were discovered after synthesis; nine compounds are synthetics that have not yet been found as minerals. In summary, 15 of the 21 ternary minerals in the $CaO$-$B_2O_3$-$H_2O$ system were discovered without knowledge of a synthetic analogue. More generally, only 55 or 19% of the 296 B minerals were synthesized prior to discovery (Table 2, Appendix 1), which suggests that synthetic compounds are not a particularly promising source for predicting potential new B minerals even if the number of synthetics is large. Moreover, 86 minerals or 29% of all B minerals have unique structures, that is, no analogues have been synthesized and the mineral is not isostructural with a known mineral and thus could not be predicted. We conclude that the realm of as yet undiscovered B minerals holds a significant number of surprises, and the same could hold for other minerals.

## APPLICATION OF THE LARGE NUMBER OF RARE EVENTS MODEL

### Impact of technology on estimating Earth's boron mineral endowment

At the rate B minerals have been discovered in the last 50 years, from over 20 to nearly 60 species every 10 years (Figs. 4, 5), the entirety of the B mineral endowment in Earth's crust would be discovered before the end of 21st century. Is such an outcome plausible? To answer this question, the mineral species/locality data for 295 of the currently recognized 296 B minerals

(Table 5) were fitted to both the finite Zipf–Mandelbrot (fZM) (Fig. 6) and the Sichel's generalized inverse Gauss-Poisson (GIGP) large number of rare event (LNRE) distributions, which gave total species counts of 459 ± 65.5 and 523, respectively—values that are similar within the standard error calculated for the fZM species count from Monte Carlo methods (Tables 6, 7). At the present rate of discovery (from >20 to 65 minerals every 10 years, Figs. 4, 5), it shouldn't take more than 100 years to discover the remaining ~200 B minerals.

However, Hazen et al. (2015a,b) and Hystad et al. (2015a,b) emphasized that the number of missing minerals could be much greater than given by the models if new procedures or protocols have been introduced since the first discoveries (i.e., the "rules of the game" were changed). The following factors deserve consideration: (1) the role of increasingly sophisticated instrumentation, particularly the electron microprobe, X-ray diffraction (both single-crystal and powder using the Rietveld method), and electron microscopy; and (2) changes in mineralogical nomenclature.

In principle, the advent of sophisticated analytical instruments should enhance the capability of discovering and characterizing new minerals. Specifically, the electron microprobe makes possible routine quantitative chemical analysis of areas as small as 20 μm across, which are too small for quantitative chemical analysis by non-electronic methods; electron microscopy enables study of minerals 2 μm or less across (e.g., qingsongite, Fig. 3D; Dobrzhinetskaya et al. 2009, 2014); and single-crystal X-ray diffraction instrumentation with high-flux sources and charge-coupled device detectors allows structural refinement of smaller crystals, e.g., nolzeite fibers 7 μm x 8 μm x 55 μm on average (Fig. 3C, Haring and McDonald 2017). We chose to evaluate the effect of the electron microprobe, because its widespread acceptance as the best analytical method occurred relatively quickly and sufficiently far back in time for its effect, if any, to be discerned, whereas advances in X-ray diffraction and widespread use of advanced electron microscopy are more recent phenomena. Although electron microprobe analyses were possible in the late-1960s (e.g., garnet, Dudley 1969), use of the electron microprobe did not exceed that of "wet" chemistry in characterizing new boron minerals until after 1978 (Fig. 2). Admittedly, this choice is to some degree arbitrary as it ignores several considerations: (1) the electron microprobe was less widely available in the late 1970s in countries such as China and the former Soviet Union, where many boron minerals had been discovered, than in the U.S., Canada, and Western Europe; (2) the electron beam can damage readily dehydrated species; and (3) quantification of boron content is difficult with the electron microprobe. However, there is another rationale for selecting 1978 – just 50% of the currently known boron minerals had been discovered by 1978, giving an even split. In view of the low resolution of the LNRE model (459 ± 65.5 species), we decided that it would not be feasible to select more than one cutoff date.

To test how the electron microprobe impacted the discovery of boron minerals, the mineral species/locality data for the 146 B minerals discovered through the year 1978 (Tables 5, 6) were fitted to both the fZM (Fig. 6) and the GIGP LNRE distributions, which gave total species counts of 306 and 359, respectively. Although we were not able to get a standard error estimate for the 1978 data set using Monte Carlo methods, we believe that several conclusions can still be drawn by comparing the accumulation curves for the 2017 and 1978 data sets (Fig. 6, Tables 6, 7). The 1978 data give lower total species counts using both distributions, and the fZM totals differ by 150 species, more than uncertainty estimated for the 2017 total. In addition, the accumulation curves for 1978 and 2017 do not coincide, which is evident by comparing the species at a given number of mineral species/locality pairs using the fZM model. The accumulation curve for the 1978 data projects 193 ± 7 species at 7024 mineral species/locality pairs, significantly less than 295 species actually recognized. Conversely, the accumulation curve for the 2017 data gives 218 ± 8 species at 3214 mineral species/locality pairs, significantly more than the observed 146 species. In other words, the discovery of new B minerals has accelerated relative to the number of mineral species/locality pairs since 1978, most plausibly from the increasing use of the electron microprobe and other instrumentation in the characterization of new boron minerals.

## Impact of grain size on estimating Earth's boron mineral endowment

Intuitively, one might expect the primary mechanism by which the electron microprobe could accelerate mineral discoveries and increase the number of potential minerals would be reduction in the size of the mineral grains accessible to study (Fig. 3). Another factor is that mineral species diversity could be fractal, that is, diversity is independent of scale and the same number of minerals can be found at the micrometer scale as at the meter scale, implying that a large number of species could be found if smaller scales were examined. The Ca-Al-rich inclusions (CAIs) in the Allende meteorite suggest a major impact of grain size – only a handful of minerals having sizes of hundreds of micrometers across constitute the bulk of the CAIs, melilite, spinel, clinopyroxene, and anorthite, whereas 16 minerals have been discovered so far at the micrometer scale (e.g., Ma and Rossman 2009; Ma et al. 2014; Ma 2015). Ma (2015) emphasized that characterizing the minerals in the CAIs, "nanomineralogy", required an integrated approach using the field-emission scanning electron microscope (FE SEM) for high-resolution electron imaging, energy dispersive spectroscopy (EDS) for reconnaissance chemical analysis, electron backscattered diffraction (EBSD) for crystal structure analysis, and the electron microprobe for quantitative chemical analysis.

Daughter phases in fluid inclusions is another realm of mineral diversity made more accessible by microbeam technology, specifically, micro-Raman spectroscopy; indeed, two new borates, ramanite-(Rb) and ramanite-(Cs) were named to mark this new capability (Thomas et al. 2008).

To evaluate a possible role of size in increasing diversity of boron minerals, a plot of the maximum volume of individual crystals or grains of new minerals in type material as a function of discovery date (Table 1 Appendix 1) reveals a broad decrease in volume with time (Fig. 7). Conspicuous exceptions to this trend are very fine grained minerals such as szaibélyite, which apparently occurs at the type locality in sufficient abundance to be separated and analyzed qualitatively (Peters 1862; Marincea 2001). Another example is "bakerite" (now discredited), which forms ultrafine-grained veins and nodules sufficiently large and pure to be analyzed quantitatively in bulk (Giles 1903). Minerals discovered after 1978 tended to be finer grained than minerals discovered prior to 1978 (Figs. 3, 8). Moreover, the number of minerals of a given size versus size for minerals discovered after 1978 increases in a broadly linear array from $10^5$ $mm^3$ to $10^{-3}$ $mm^3$ on a log-log plot, and then drops sharply at finer sizes; such a pattern is not evident in the pre-1978 data (Fig. 8). The quasi-linear trend suggests an approximation to a power-law relationship between $10^5$ $mm^3$ and $10^{-3}$ $mm^3$. In other words, sizes of new mineral discoveries could be fractal at sizes between $10^{-3}$ $mm^3$ and $10^5$ $mm^3$, and the number of potential new minerals (i.e., the total population), should increase as the scale of search is extended to smaller and smaller volumes. The electron microprobe, together with the other electron microbeam technologies cited by Ma (2015), has opened up a whole new realm of species diversity. This new realm could explain the acceleration of discoveries evident in comparing the accumulation curves for the 2017 and 1978 data sets. Whether fractal distribution can be expected at smaller and smaller volumes is an open question – could $10^{-3}$ $mm^3$ be a limiting minimum sample volume for diversity to be fractal as suggested by the steep drop off in the number of minerals smaller than $10^{-3}$ $mm^3$? In any case there is a natural limit imposed by the minimum number of unit cells needed to recognize a compound as a distinct phase.

## Impact of anthropogenic minerals

Hazen et al. (2017, Table 1A) identified 91 minerals that are known or suspected to form exclusively as byproducts of human activities. This list includes four B minerals: canavesite, $Mg_2(HBO_3)(CO_3)\cdot 5H_2O$, which formed on mine tunnel walls at the Brosso mine, Piedmont, Italy (type, Ferraris et al. 1978) and the Sterling Mine, Sussex County, New Jersey, USA (Dunn 1995), ammonioborite, biringuccite, and nasinite, The last three are borates associated with geothermal piping systems at Larderello, Tuscany, Italy, and were discovered prior to 1978; none have been reported from another locality. Four other B minerals occur both as an inadvertent human-mediated phase and as a natural phase (Hazen et al. 2017, Table 1B). Given that only four B minerals are exclusively anthropogenic, the impact of anthropogenesis is considered to be negligible on the estimates of total potential B mineral species.

## Impact of mineral nomenclature on estimating Earth's boron mineral endowment

Change in mineral nomenclature is the second factor that potentially has a major impact on the LNRE models. The concept of a mineral species has evolved with time, and the present-day criteria for distinguishing species were set out by the CNMNC IMA only about 20 years ago (e.g., Nickel 1992; Nickel and Grice 1998), and refinements continue, for example, Hatert and Burke (2008). Overall, the changes have resulted in ever-increasing division of compositional space, resulting in increased numbers of new species. This development is exemplified by the tourmaline supergroup, which is the only group (or supergroup) of B minerals affected. For example, Dana (1892) considered tourmaline as a single species with numerous varieties such as "ordinary," "dravite of Tschermak," and "rubellite." Winchell (1949) interpreted tourmaline as a single species with a very broad range of composition comprising 3 subspecies, later increased to 5 in his textbook (Winchell and Winchell 1951). In contrast, Strunz and Tennyson (1982) recognized a "Turmalin-Reihe" (tourmaline-series) with 5 confirmed and one hypothetical species. Hawthorne and Henry (1999) proposed a classification for a tourmaline group with 13 species broadly consistent with CNMNC principles (Nickel 1992), but they did not submit the proposal to the Commission for approval, preferring to wait for completion of ongoing studies of tourmaline-group minerals. CNMNC IMA approval and publication of a far more detailed and comprehensive version of this classification (Henry et al. 2011) took 12 years. It comprised 14 species approved prior to approval of the classification (one more than approved prior to 1999) and 5 approved at roughly at the same time, yielding a total of 18 approved species, although several were published after the classification. Now there are 32 approved species, as the nomenclature has stimulated a search for new tourmaline species.

However, not all of the new species are as distinct from pre-existing species as species recognized before 1999 are from one another. Tourmaline has 5 cation sites and two anion sites; a generalized formula is $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, where B, the boron site, is occupied only by this element. Compositions of the 13 species in the 1999 classification differ significantly in occupancy of the 9-coordinated X-site or the octahedrally-coordinated Y and Z sites considered together. The 2011 classification directed attention to more subtle compositional differences that had received little attention before 2011, notably occupancy of the anionic W-site; single-crystal X-ray diffraction has become an important method to document these distinctions. Five new species are based on F versus OH at W, and 5 others on O versus OH at this site. Substitution of O for OH requires changes in cation composition at the X, Y and Z sites to balance charge, but these changes are small compared to the differences among the 13 species in the 1999 classification. Another subtle distinction is between the new species adachiite, $CaFe^{2+}{}_3Al_6(Si_5AlO_{18})(BO_3)_3(OH)_3(OH)$, and the pre-existing species feruvite, $CaFe^{2+}{}_3(Al_5Mg)(Si_6O_{18})(BO_3)_3(OH)_3(OH)$, which differ in the exchange ${}^{T}Si + {}^{Z}Mg$ (ferruvite) → ${}^{T}Al + {}^{Z}Al$ (adachiite), which would be difficult to establish with only an electron microprobe analysis. Thus, of 20 species discovered since 1999, we conclude that no more than 8 are as distinct from one another and from pre-existing species as the 13 described earlier. In other words, relatively subtle differences formulated in the new nomenclature contributed significantly to the marked upsurge in new tourmaline species.

This new diversity could also have contributed to the acceleration of discoveries evident in comparing the accumulation curves for the 2017 and 1978 data sets that we attributed to the access to finer grain sizes through use of the electron microprobe.

### Impact of targeted searches and the internet

Another consideration is that the LNRE models presume that the discovery of minerals is stochastic. However, there is evidence that in some cases new minerals have been specifically sought. For example, the spike in new B minerals in the early 1960s could reflect non-randomness: 14 of the 36 minerals discovered over the 10-year period from 1957 to 1966 were reported from the former USSR, which suggests a targeted search for B minerals as source of strategic material. Another non-random discovery occurs when synthesis of a compound leads to the search for a natural analogue, e.g., pseudosinhalite (Schreyer et al. 1998). More recently, a purposeful search for new tourmaline species following approval of the tourmaline-supergroup nomenclature resulted in a jump of new tourmalines. In contrast to the other factors discussed above, there were targeted searches both before and after 1978, and it is reasonable to assume as a first approximation that such non-randomness impacted new mineral discoveries as much before 1978 as afterwards. Indeed, if the present paper on the projected discovery of new boron minerals were to lead to new targeted searches for specific species, then it could alter the projected numbers of boron minerals.

A related consideration is the increasingly more rapid and voluminous exchange of information and improved capabilities of communication afforded by the internet, which has undoubtedly accelerated the pace at which new minerals can be characterized. In effect, technological advances can be shared by a greater number of investigators through collaborations.

## IMPLICATIONS

In principle, LNRE models hold great promise in providing an estimate of the total endowment of B minerals in Earth's crust based on the number of minerals found to date. However, the increasing pace at which B minerals are discovered seems to be at odds with limits on total mineral diversity implied by the LNRE model. Because changes in how new minerals are characterized could impact the model, as argued by Hazen et al. (2015a,b) and Hystad et al. (2015a,b), we have quantitatively evaluated the robustness of the LNRE estimates by comparing the accumulation curve based on minerals discovered by 1978, when the electron microprobe became the dominant analytical method for characterizing B minerals and when 50% of the presently known boron minerals had been discovered, with the accumulation curve based on all 295 boron minerals discovered to date (2017). Since 1978, technological advances in other instrumentation for characterizing new minerals, notably single-crystal X-ray diffractrometry, micro-Raman spectroscopy, and electron microscopy, which, in tandem with electron microprobe analyses, have increased our capability for working with ever smaller grains and amounts. If the occurrence of minerals followed a fractal pattern, there could be as much species diversity at the nanometer to micrometer scale as at larger scales. In addition, changes in the definition of mineralogical species have led to an increased potential for species diversity. In other words, the "rules of the game" have been changed since 1978, so that estimated populations inferred from the rules in effect prior to 1978 are no longer appropriate for the number of species inferred when minerals discovered under the new set of rules are included in the mix. Consequently, it is not surprising that estimates of the total endowment from LNRE models for 1978 are significantly less than the estimates for 2017. Our comparison of the 1978 and 2017 datasets is the first test of its kind in application of LNRE models to minerals, and it indicates that these models are impacted by changes in the definition of a mineral species, in the range of workable sizes of new minerals, and in the instrumentation used to characterize new minerals. The impact is significant, increasing the estimated total endowment by 50% from 1978, whether the fZM or GIGP distribution is applied (Table 7). The ~500 B species estimate from the 2017 data is undoubtedly not the end of the story, as we can count on further technological advances (together with wider use of existing highly advanced technologies) in the future even if the definition of a mineral species stabilizes. A more realistic finale might come when we reach the natural limit imposed by the minimum number of unit cells needed for new mineral to be viable. If our descendants were to try LNRE modeling when the natural limit is reached, they might get an estimate closer to the true endowment, and show that, after all, Earth's total endowment of B minerals is finite.

That 41% of boron minerals could not have been predicted at the time of discovery from existing minerals or from prior syntheses suggests that surprises are likely in future studies of boron minerals; indeed, mineralogical studies in general could yield a treasure trove of unexpected compounds. Similarly, the unpredictable could play a significant role in mineralogical investigations of other planetary bodies. To date, this potential for novelty has not been realized for the Moon, where relatively few minerals are new compounds, even at the time of discovery (Hazen et al. 2015a and references cited therein), but might apply to Mars, which has been subjected to extensive weathering due the presence of an atmosphere, and the moons of Jupiter and Saturn, which have such exotic chemistries.

## DEDICATION

We dedicate this paper to Nikolai Nikolayevich Pertsev, who died May 21, 2016 at 85 years of age. Pertsev devoted his career to boron minerals, culminating in publication of his monograph "Parageneses of Boron Minerals in Magnesian Skarns" (Pertsev 1971). Nikolai Nikolayevich was ESG's host in Moscow for his interacademy exchanges to the former USSR, when Nikolai Nikolayevich arranged for expeditions to the Aldan Shield (1987) and southwestern Pamir Mountains (1990) in search of kornerupine and prismatine. For many years, Nikolai Nikolayevich provided ESG with hard to get references and information on occurrences of B minerals in the former USSR that has proved invaluable for ESG's research.

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Zeigan, D. (1967) Zur Struktur einer neuen Modifikation von Calcium (1:1:4)-borathydrat. Zeitschrift für Chemie, 7(6), 241-241.

Table 4. Ternary compounds in the $CaO-B_2O_3-H_2O$ system for which crystallographic data are available

| Mineral | Chemical formula | Space group | Date (mineral) | Date (synthesis) | References for structure (mineral) | References for synthesis and structure of synthetic |
|---|---|---|---|---|---|---|
| Alfredstelznerite | $Ca_4(H_2O)_4(B_4O_4(OH)_6)_4(H_2O)_{15}$ | $Pca2_1$ | 2010 | — | Cooper et al. (2010) | — |
| Colemanite | $Ca(B_3O_4(OH)_3)(H_2O)$ | $P2_1/a$ | 1883 | 1906 | Christ et al. (1958); Clark et al. (1964); Burns and Hawthorne (1993a) | Palache et al. (1951); van't Hoff (1906) |
| Fabianite | $Ca(B_3O_5)(OH)$ | $P2_1/a$ | 1962 | — | Konnert et al. (1970) | — |
| — | $Ca(B_3O_5)(OH)$ | $Pba2_1$,<br>$Pbn2_1$ | — | — | — | Clark et al. (1962); Clark et al. (1964); Yamnova et al. (2015) |
| Frolovite | $Ca(B(OH)_4)_2$ | P-1 | 1957 | 1907 | Egorov-Tismenko et al. (1972); Simonov et al. (1976a) | Meyerhoffer and van't Hoff (1907); Zeigan (1966) |
| — | $Ca(B(OH)_4)_2$ | P2/c | — | — | — | Zeigan (1966, 1967) |
| — | $Ca(B(OH)_4)_2$ | $Pban$ | — | — | — | Zeigan (1966, 1967) |
| Ginorite | $Ca_2B_{14}O_{20}(OH)_6 \cdot 5H_2O$ |  | 1934 | 1970 | Pankova et al. (2016) | Nekrasov et al. (1970) |
| Gowerite | $Ca(B_5O_8(OH))(B(OH)_3)(H_2O)_3$ | $P2_1/a$ | 1959 | 1949 | Konnert et al. (1972) | Erd et al. (1959) ; Lehmann et al. (1966) |
| Hexahydroborite | $Ca(B(OH)_4)_2(H_2O)_2$ | $P2/c$* | 1977 | 1907 | Simonov et al. (1976b) | Meyerhoffer and van't Hoff (1907); Ozol et al. (1964); Yamnova et al. (2011) |
| — | $Ca(B(OH)_4)_2(H_2O)_2$ | $C2/c$ | — | — | — | Kravchenko (1964); Sedlacek and Dornberger-Schiff (1971); Yamnova et al. (2011) |
| Inyoite | $Ca(B_3O_3(OH)_5)(H_2O)_4$ | $P2_1/a$,<br>$P2_1/c$ | 1914 | 1938 | — | Nikolayev and Chelishcheva (1938); Clark (1959); Clark et al. (1964) |
| Jarandolite | $Ca(B_3O_4(OH)_3)$ | $P2_1/a$ | 2004 | — | Yamnova et al. (1994) | — |
| Korzhinskite | $Ca(B_2O_4) \cdot H_2O$ |  | 1963 | 1970 | structure not refined | Nekrasov et al. (1970); Nekrasov (1973); Dimitrova et al. (2006) |
| Meyerhofferite | $Ca(B_3O_3(OH)_5)(H_2O)$ | $P$-1 | 1914 | 1907 | Burns and Hawthorne (1993b) | Meyerhoffer and van't Hoff (1907); Christ and Clark (1960); Clark and Christ (1960); Clark et al. (1964) |
| Nifontovite | $Ca_3(B_3O_3(OH)_6)_2(H_2O)_2$ | $B2/b$ | 1961 | — | Egorov-Tismenko et al. (1973a); Simonov et al. (1978) | — |
| Nobleite | $Ca(B_6O_9(OH)_2)(H_2O)_3$ | $P2_1/a$ | 1961 | 1873 | Karanović et al. (2004) | Ditte (1873); Erd et al (1961); Lehmann et al. (1966) |
| Olshanskyite | $Ca2(B_3O_3(OH)_6)(OH)(H_2O)_3$ | $P$-1 | 1969 | 2007 | Callegari et al. (2001) | Wang et al. (2007) |
| Parasibirskite | $CaHBO_3$ | $P2_1/m$ | 1998 | 1958 | Takahashi et al. (2010) | Lehmann et al. (1958); Sun et al. (2011) |
| Sibirskite | $CaHBO_3$ | $P2_1/a$,<br>$P2_1/c$ | 1962 | 1970 | Miura and Kusachi (2008) | Nekrasov et al. (1970); Sun et al. (2011) |
| Pentahydroborite | $Ca(B_2O(OH)_6)(H_2O)_2$ | $P$-1 | 1961 | — | Egorov-Tismenko et al. (1973b); Kazanskaya et al. (1977) | — |
| Priceite | $Ca_2(B_5O_7)(OH)_5(H_2O)$ | $P2_1/c$ | 1873 | 1970 | Wallwork et al. (2002) | Nekrasov et al. (1970); Sun et al. (2011) |
| Tyretskite | $Ca_2B_5O_9OH \cdot H_2O$ |  | 1958 | — | Kondrat'eva (1964); Davies and Manchin (1968) | — |
| Uralborite | $Ca(B_2O_2(OH)_4)$ | $P2_1/n$ | 1961 | — | Shashkin et al. (1970); Simonov et al. (1977) | — |
| Vimsite | $Ca(B_2O_2(OH)_4)$ | $C2/c$,<br>$B2/b$ | 1968 | 1973 | Shashkin et al. (1968); Simonov et al. (1976c) | Nekrasov (1973) |

| | | | | | | |
|---|---|---|---|---|---|---|
| — | $CaB_3O_3(OH)_5(H_2O)_2$ | *P*-1 | — | — | — | Clark and Christ (1957, 1959); Clark et al. (1964) |
| — | $Ca_2(B_8O_{13}(OH)_2)$ | *P*-1 | — | — | — | Nekrasov et al. (1970); Simonov et al. (1975); Yamnova et al. (1976) |
| — | $Ca(B_5O_8(OH))(H_2O)$ | $P2_1/c$ | — | — | — | Yamnova et al. (2003) |
| — | $Ca(B_8O_{11}(OH)_4)$ | $P2_1$ | — | — | — | Nekrasov et al. (1970); Zayakina and Brovkin (1978); Yamnova et al. (2005); Wiggin and Weller (2005) |
| — | $Ca_2(B_5O_8(OH))_2B(OH)_3(H_2O)$ | *P*1 | — | — | — | Yamnova et al. (2009) |

Note: Date of synthesis is given only for synthetic analogues of known minerals. * transformed to standard setting

Table 5. Number of minerals found at a given number of localities in 2017 and in 1978 used as input for large number of rare events modeling

| Localities 2017 | Minerals 2017 | Localities 1978 | Minerals 1978 |
|---|---|---|---|
| 1 | 105 | 1 | 57 |
| 2 | 46 | 2 | 17 |
| 3 | 34 | 3 | 16 |
| 4 | 11 | 4 | 5 |
| 5 | 16 | 5 | 7 |
| 6 | 4 | 6 | 3 |
| 7 | 5 | 7 | 8 |
| 8 | 7 | 8 | 2 |
| 9 | 4 | 9 | 1 |
| 10 | 3 | 10 | 2 |
| 11 | 4 | 11 | 2 |
| 12 | 5 | 12 | 2 |
| 13 | 4 | 13 | 1 |
| 14 | 3 | 14 | 0 |
| 15 | 4 | 15 | 0 |
| 16 | 2 | 16 | 1 |
| 17 | 2 | 17 | 1 |
| 18 | 1 | 19 | 2 |
| 19 | 2 | 20 | 2 |
| 20 | 1 | 26 | 1 |
| 21 | 1 | 27 | 1 |
| 22 | 3 | 30 | 1 |
| 23 | 1 | 35 | 1 |
| 24 | 1 | 37 | 1 |
| 25 | 1 | 39 | 1 |
| 32 | 1 | 41 | 1 |
| 38 | 1 | 66 | 1 |
| 40 | 1 | 67 | 1 |
| 42 | 1 | 71 | 1 |
| 45 | 1 | 73 | 1 |
| 51 | 2 | 109 | 1 |
| 53 | 1 | 124 | 1 |
| 62 | 1 | 236 | 1 |
| 70 | 1 | 244 | 1 |
| 73 | 1 | 283 | 1 |
| 78 | 1 | 1223 | 1 |
| 79 | 1 | | |
| 80 | 1 | | |
| 82 | 1 | | |
| 132 | 1 | | |
| 134 | 1 | | |
| 142 | 1 | | |

| | | | |
|---|---|---|---|
| 146 | 1 | | |
| 218 | 1 | | |
| 247 | 1 | | |
| 471 | 1 | | |
| 487 | 1 | | |
| 565 | 1 | | |
| 2443 | 1 | | |
| | | Totals | |
| 7024 | 295 | 3214 | 146 |

Note: The total for localities is the sum of localities multiplied by the number of minerals at this number of localities. Based on data in Table 1 (Appendix 1). N.B. “Bakerite” has not been included in the 1978 list although considered valid at the time, and the unnamed $CO_3$-rich charlesite has not been included in the 2017 list.

Table 6. Parameters for the Large Number of Rare Events models.

| Data set | 2017 | 1978 |
|---|---|---|
| finite Zipf-Mandelbrot LNRE model | | |
| Shape (α) | 0.5508606 | 0.4602962 |
| Lower cutoff (A) | 3.939025e-05 | 3.089639e-05 |
| Upper cutoff (B) | 0.1953747 | 0.2295875 |
| Normalization (C) | 0.99560746 | |
| Population size | 459 | 306 |
| No. of first spectrum elements | 4 | 6 |
| chi-squared | 9.074704 | 4.45118 |
| df | 5 | 3 |
| p-value | 0.1061213 | 0.2166865 |
| Standard error | 65.5 | — |
| Sichel's generalized inverse Gauss-Poisson (GIGP) LNRE model | | |
| Shape (γ) | -0.6072923 | -0.4760835 |
| Lower decay (B) | 0.02096799 | 0.01709155 |
| Upper decay (C) | 0.3282042 | 0.2830321 |
| Population size | 523 | 359 |
| No. first spectrum elements | 12 | 5 |
| chi-squared | 9.655407 | 4.074684 |
| df | 6 | 3 |
| p-value | 0.1399339 | 0.2535117 |

Note: Standard error was calculated using Monte Carlo methods. It could not be calculated for the 1978 data since the data would not converge when running Monte Carlo simulations.

Table 7. Comparison of the predicted minerals at a given number of mineral species/locality pairs between the 1978 and 2017data sets.

| | minerals | *N* | minerals | *N* | fZM total | GIGP total |
|---|---|---|---|---|---|---|
| Year | 2017 | 2017 | 1978 | 1978 | | |
| 2017 data | **295** | **7024** | 218 ± 8 | **3214** | 459 ± 65.5 | 523 |
| 1978 data | 193 ± 7 | **7024** | **146** | **3214** | 306 | 359 |

Note: N = number of mineral species/locality pairs. Bold – input from Table 5. The number of minerals and standard deviations for these numbers were calculated from equations 8 and 13, respectively, for the accumulation curves in Hystad et al. (2015a). Uncertainty in total minerals was calculated from Monte Carlo methods.

## FIGURE CAPTIONS

Figure 1. Plot of submissions of new mineral proposals and approvals of new minerals by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification in a given year. Data for the period 1962-2002 were compiled by Marco Pasero (personal communication) and for period 2003-2015 were taken from the newsletters published by the Commission up through #35 ( 2017). Withdrawn submissions and discreditations of approved species have not been deducted from the submissions.

Figure 2. Plot of the number of boron minerals characterized with the electron microprobe and by wet chemistry. First used in 1974 (bonaccordite, De Waal and Calk 1973; De Waal et al. 1974), the electron microprobe became more widely used for analyzing boron minerals after 1978. Compositions based on electron microprobe analyses for most constituents and on wet chemical data for $B_2O_3$ and/or $H_2O$ were counted as 0.5 for each method, whereas ion microprobe data for $B_2O_3$ were counted as 1.0 for the electron microprobe.

Figure 3. A. Colorless single-crystal tetrahedron of boracite ($Mg_3B_7O_{13}Cl$) with minor cube faces from Douglashall, Westereglen, Stassfurt District, Saxony-Anhalt, Germany. Werner (1789) reported that chemical analysis gave boric acid in boracite. Photograph R070317 is reproduced with permission of Robert T. Downs from the RRUFF Project (Lafuente et al. 2015). B. Colorless cleavage fragment of kernite ($Na_2B_4O_6(OH)_2 \cdot 3H_2O$) from Boron, Kern County, California. Characterization of this borate involved wet chemical analyses (Schaller 1927). Photograph R050661 is reproduced with permission of Robert T. Downs from the RRUFF Project (Lafuente et al. 2015). C. Felt-like aggregate of acicular nolzeite (Nlz, $NaMn_2[Si_3BO_9](OH)_2 \cdot 2H_2O$) with analcime (Anl), aegirine (Aeg) and nepheline (out of view)

from Mont Saint-Hilaire, Quebec, Canada. Individual nolzeite crystals average 5 x 8 x 55 μm, which precluded structure determination using standard single crystal diffractometers with scintillation detectors; instead a APEX-II charge coupled device detector was used (Haring and McDonald 2017). Photograph is reproduced with permission of Monika M. M. Haring and Andrew M. McDonald; it has been modified from Haring and McDonald (2017, Figure 1). D. Transmitting electron microscope bright-field image of qingsongite (cBN) enclosed in osbornite (TiN) surrounded by coesite (Coe) from an inclusion in chromite ore in the Luobusa ophiolite, Tibet, China (Dobrzhinetskaya et al. 2009, 2014). Composition of the nitrides was determined from elements mapped by electron dispersive spectroscopy. Image is reproduced with permission of Larissa F. Dobrzhinetskaya; it has been modified from Dobrzhinetskaya et al. (2009, Figure 4a).

Figure 4. Plot showing variation in numbers of boron minerals discovered (including potential minerals) per 10-year interval (i.e., 2008-2017, 1998-2007, etc.) before and after synthesis as a function of the year of discovery. Variation in the number of boron minerals discovered is shown for comparison. Based on data in Table 2 (Appendix 1).

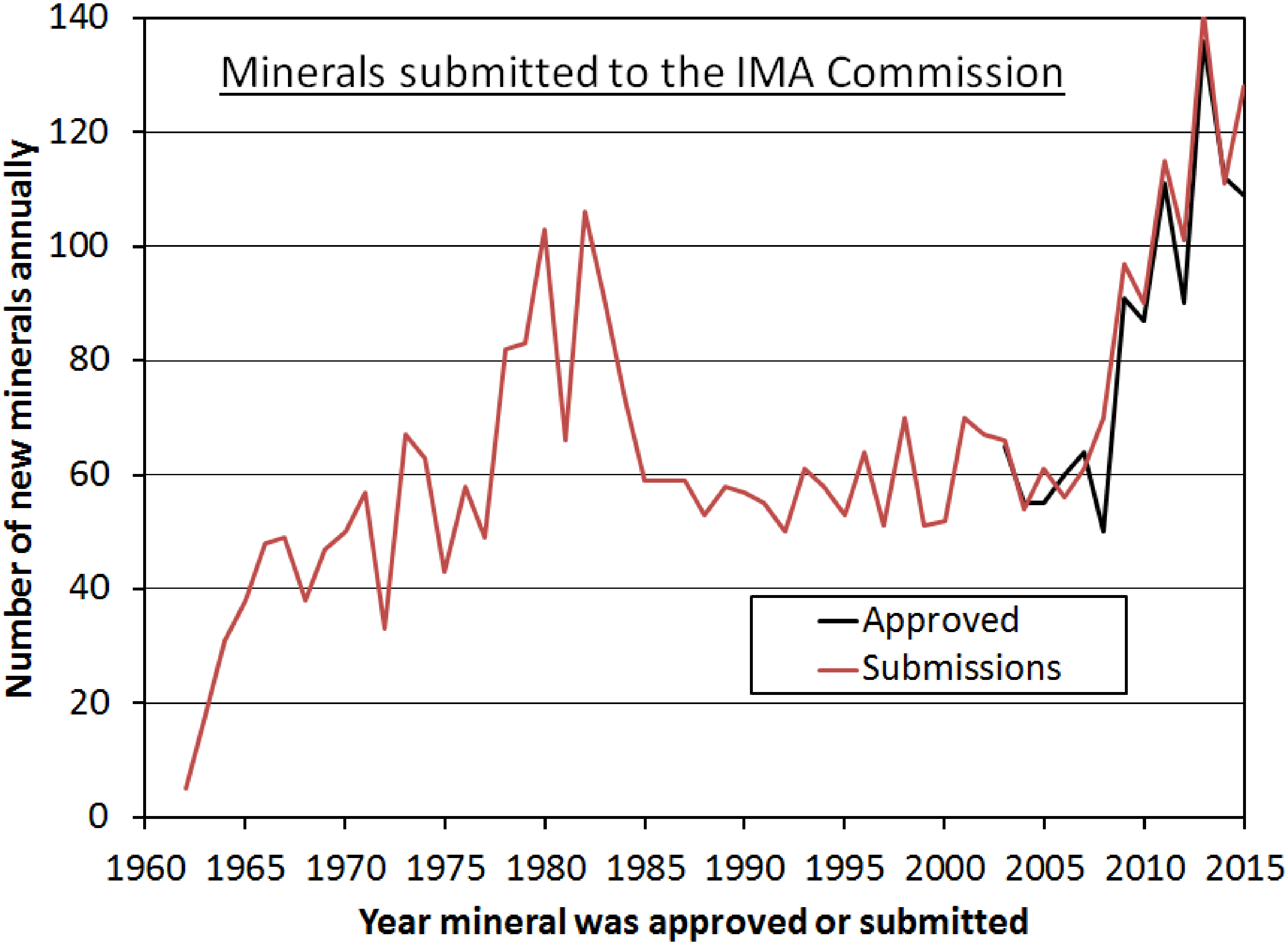
Figure 5. Plot showing variation in numbers of boron minerals discovered (including potential minerals) per 10-year interval (i.e., 2008-2017, 1998-2007, etc.) having unique crystal structures or having either solid solution or isostructural relationship with other minerals as a function of the year of discovery. Variation in the number of boron minerals discovered is shown for comparison. Based on data in Table 2 (Appendix 1).

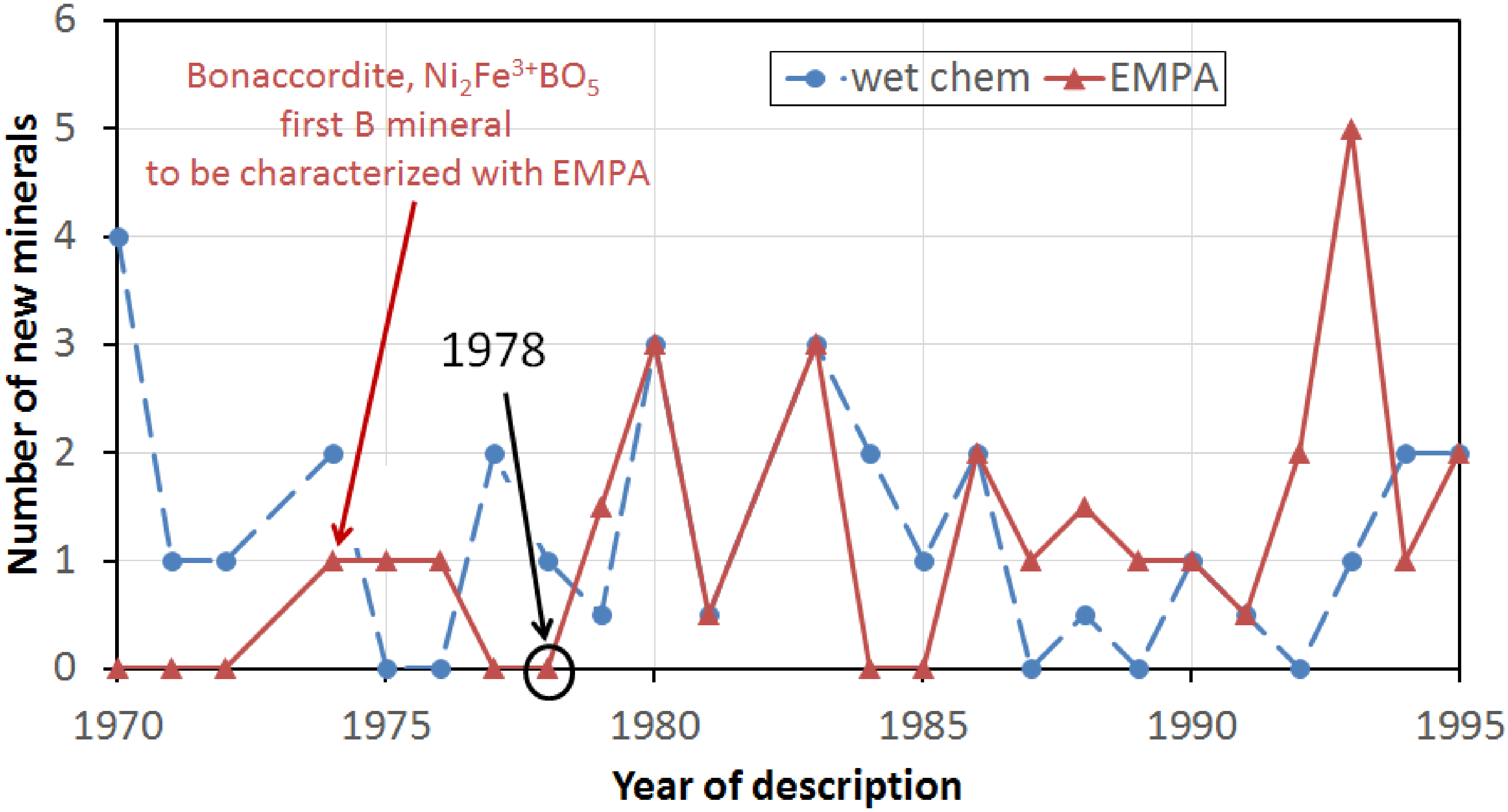
Figure 6. Accumulation curves and frequency spectra for 295 of the 296 boron minerals recognized in 2017 and for the 146 boron minerals recognized in 1978. The curves are based on

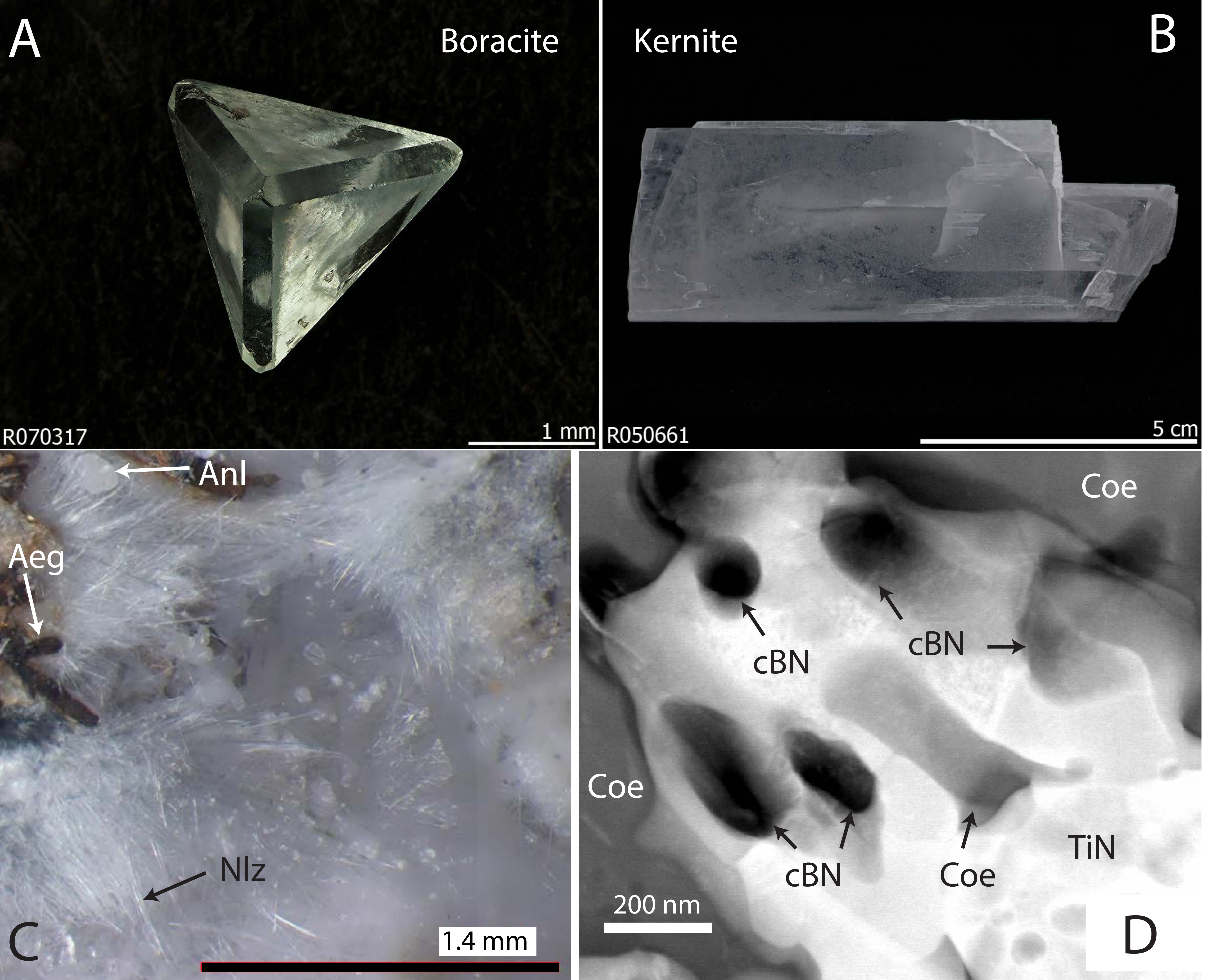
the fZM model using the data in Table 5, which summarizes Table 1 (Appendix 1). The standard errors were estimated by Monte Carlo methods (Table 6).

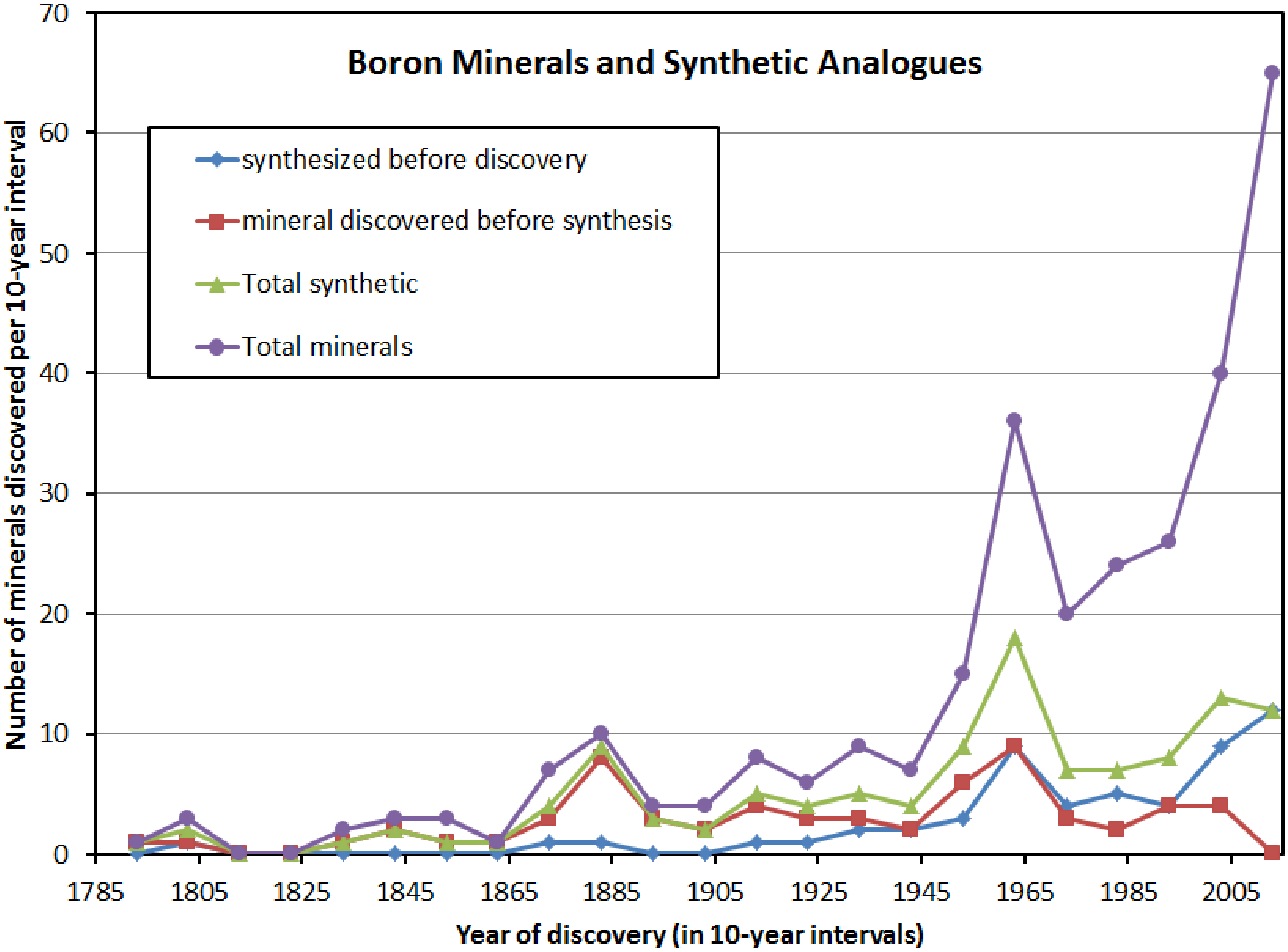
Figure 7. Plot of volumes of new minerals (holotype material) and potential minerals as a function of the year of discovery. Volume was taken from maximum dimensions reported for individual grains or crystals. "Bakerite" (now discredited) and szaibélyite are notable exceptions to the overall trend of decreasing grain size with time ("bakerite" grains are estimated to be on the order of a micrometer in type material, Anthony Kampf, personal communication). Based on data in Table 1 (Appendix 1).

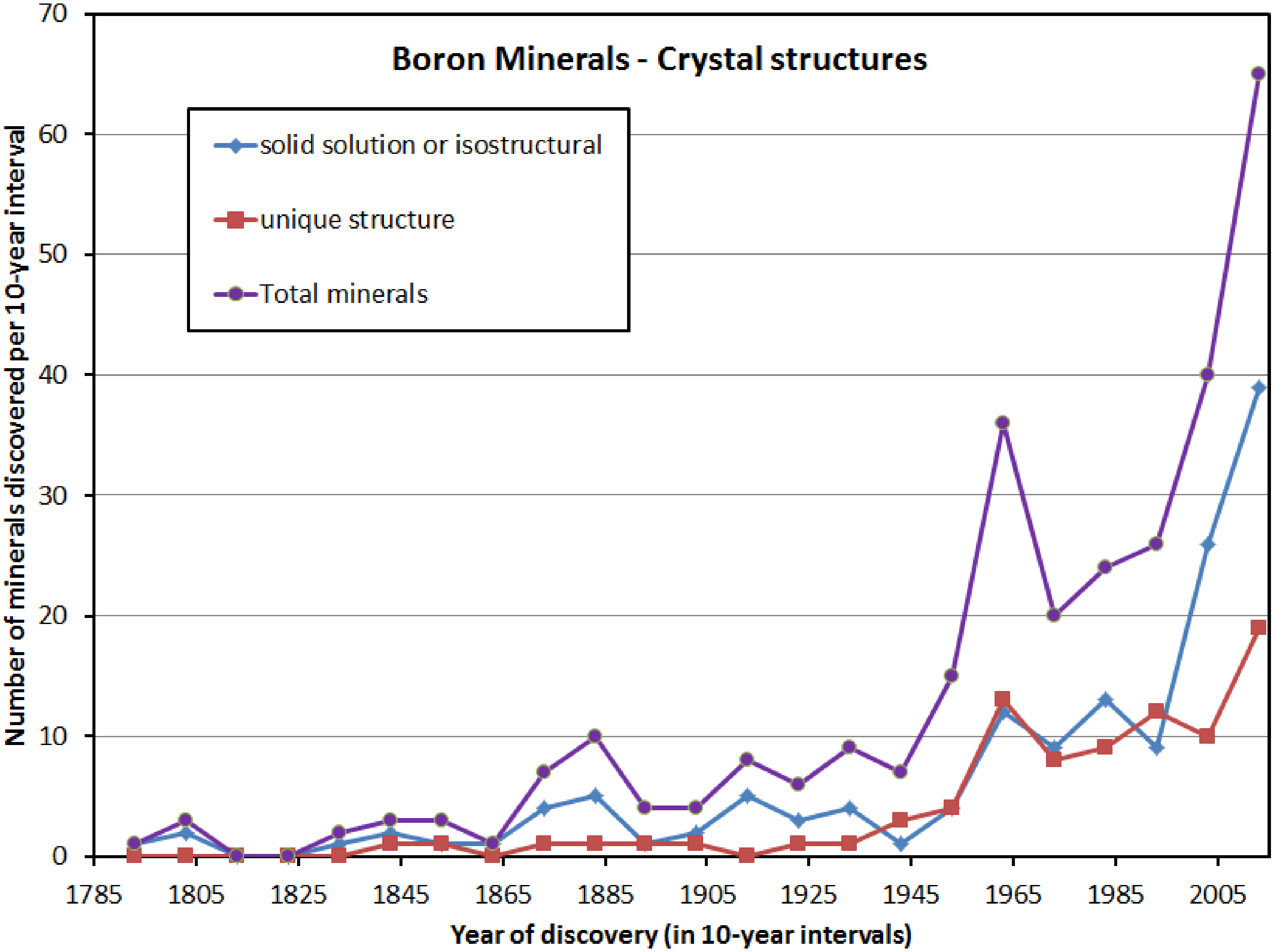
Figure 8. Plot of number of new minerals (holotype material) and potential minerals having a given range of grain volume (bin size – 1 log unit). Volume was taken from maximum dimensions reported for individual grains or crystals. Based on data in Table 1 (Appendix 1).

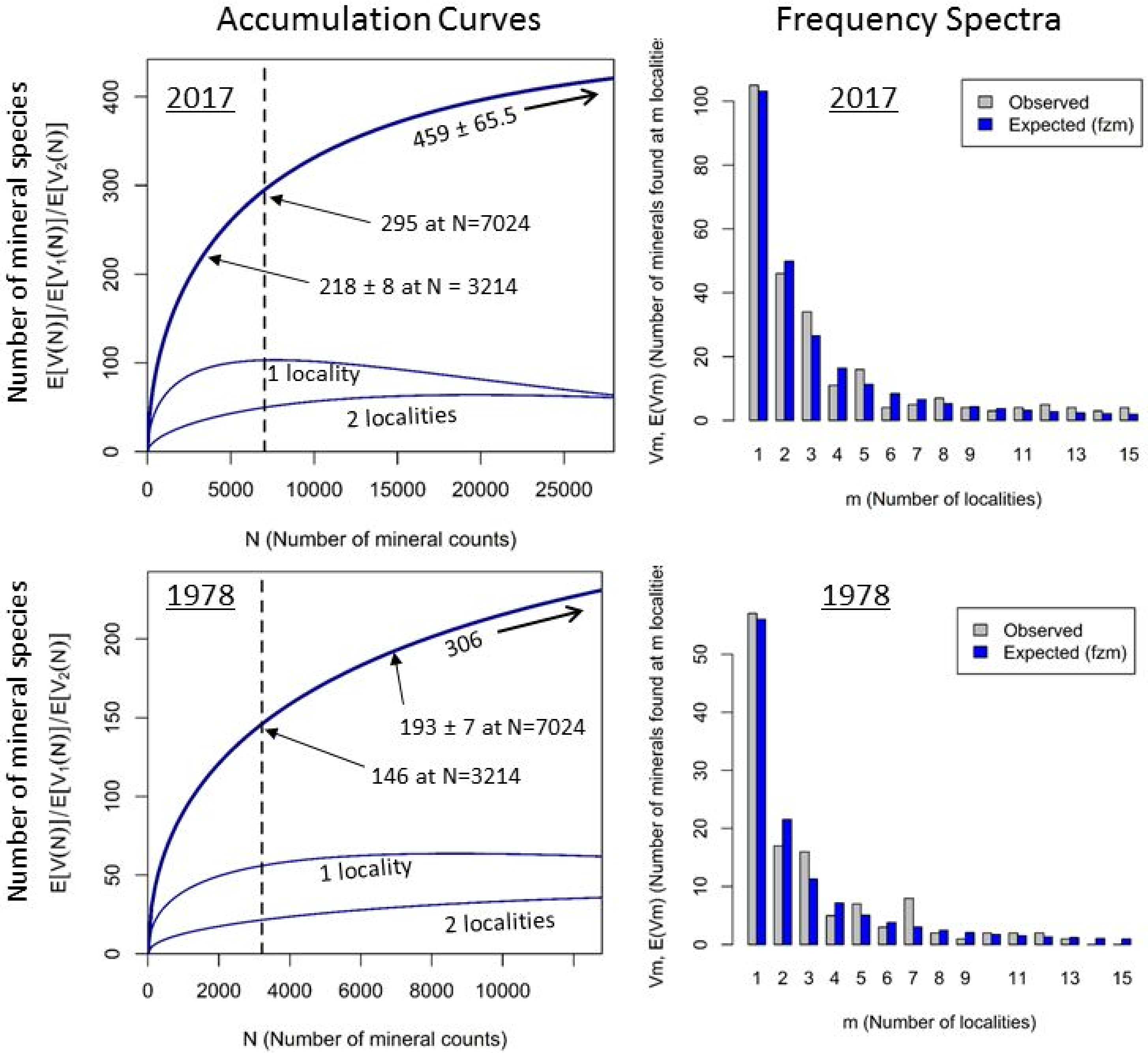

Minerals submitted to the IMA Commission
Number of new minerals annually
0
20
40
60
80
100
120
140
1960
1965
1970
1975
1980
1985
1990
1995
2000
2005
2010
2015
Year mineral was approved or submitted
Approved
Submissions

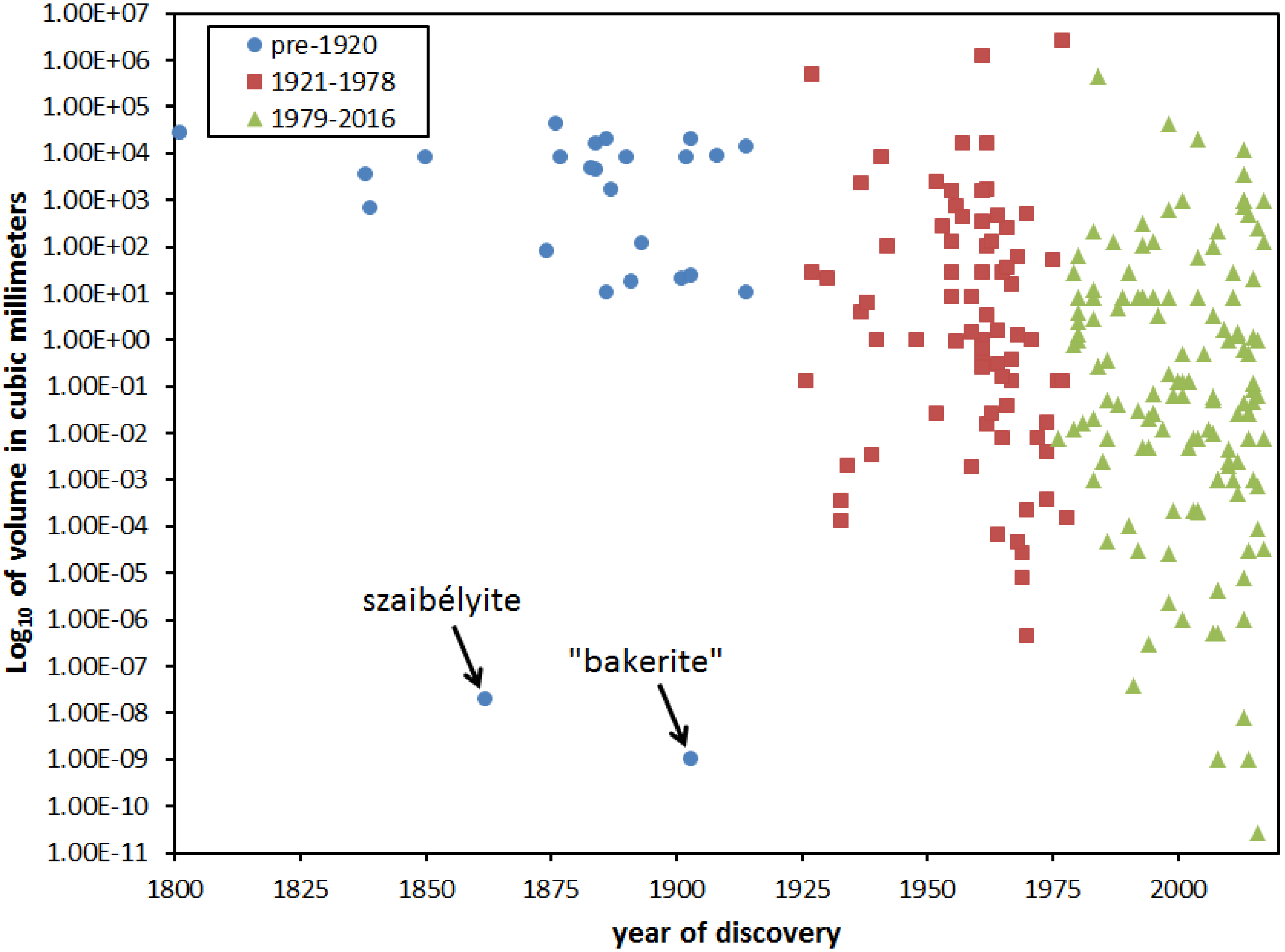

Bonaccordite, $Ni_2Fe^{3+}BO_5$
first B mineral
to be characterized with EMPA
1978
wet chem
EMPA
Number of new minerals
Year of description
0
1
2
3
4
5
6
1970
1975
1980
1985
1990
1995


A
Boracite
R070317
1 mm
Kernite
B
R050661
5 cm
Anl
Aeg
Nlz
1.4 mm
C
Coe
cBN
cBN
Coe
cBN
Coe
TiN
200 nm
D

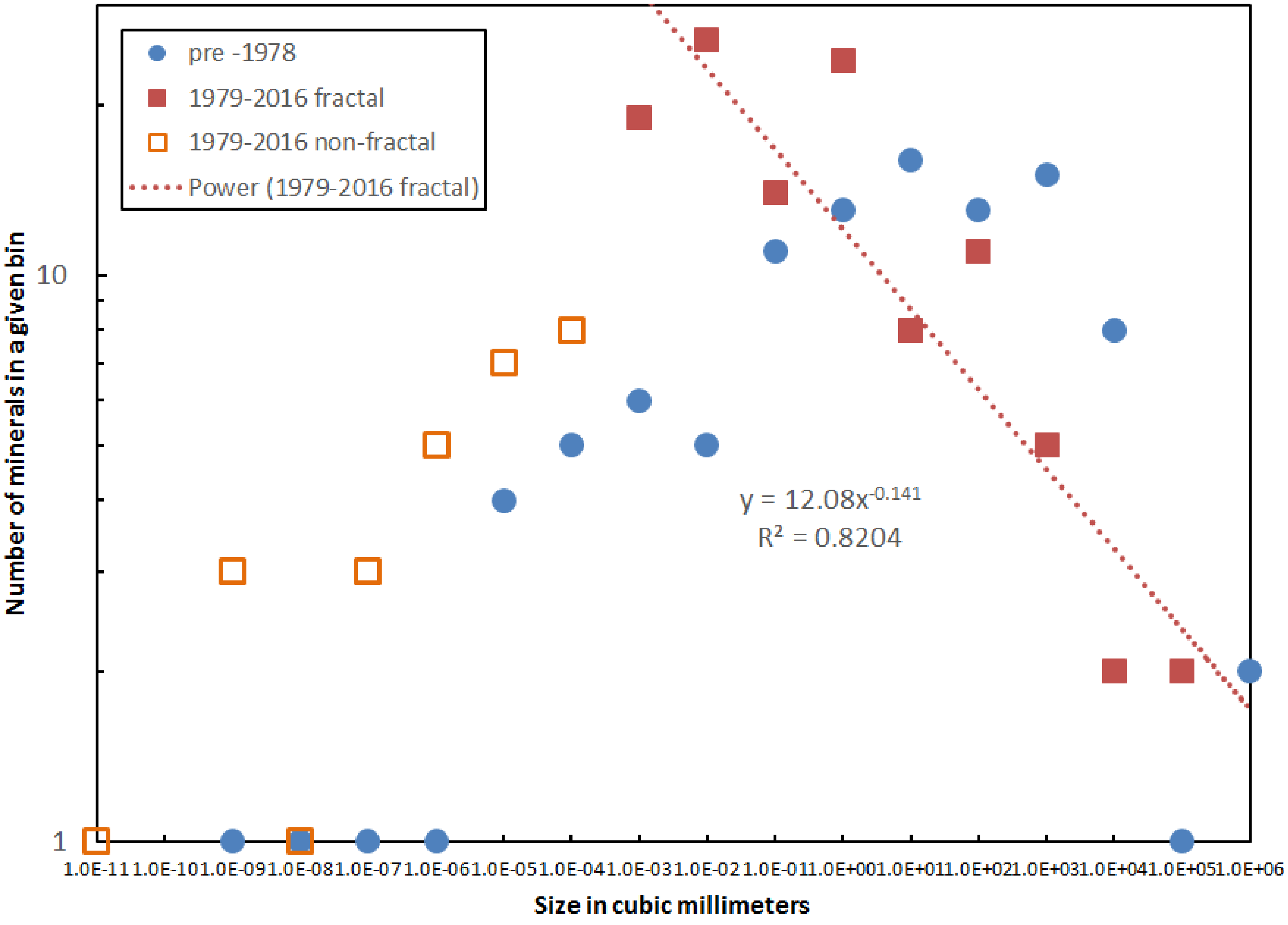

Boron Minerals and Synthetic Analogues
synthesized before discovery
mineral discovered before synthesis
Total synthetic
Total minerals
Number of minerals discovered per 10-year interval
Year of discovery (in 10-year intervals)
0
10
20
30
40
50
60
70
1785
1805
1825
1845
1865
1885
1905
1925
1945
1965
1985
2005


Boron Minerals - Crystal structures
solid solution or isostructural
unique structure
Total minerals
Number of minerals discovered per 10-year interval
Year of discovery (in 10-year intervals)
0
10
20
30
40
50
60
70
1785
1805
1825
1845
1865
1885
1905
1925
1945
1965
1985
2005


Accumulation Curves
Frequency Spectra
2017
Number of mineral species
E[V(N)]/E[V1(N)]/E[V2(N)]
0
100
200
300
400
459 ± 65.5
295 at N=7024
218 ± 8 at N = 3214
1 locality
2 localities
0
5000
10000
15000
20000
25000
N (Number of mineral counts)
2017
Observed
Expected (fzm)
Vm, E(Vm) (Number of minerals found at m localitie
0
20
40
60
80
100
1
2
3
4
5
6
7
8
9
11
13
15
m (Number of localities)
1978
Number of mineral species
E[V(N)]/E[V1(N)]/E[V2(N)]
0
50
100
150
200
306
193 ± 7 at N=7024
146 at N=3214
1 locality
2 localities
0
2000
4000
6000
8000
10000
N (Number of mineral counts)
1978
Observed
Expected (fzm)
Vm, E(Vm) (Number of minerals found at m localitie
0
10
20
30
40
50
1
2
3
4
5
6
7
8
9
11
13
15
m (Number of localities)



1.00E+07
1.00E+06
1.00E+05
1.00E+04
1.00E+03
1.00E+02
1.00E+01
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
1.00E-07
1.00E-08
1.00E-09
1.00E-10
1.00E-11
Log$_{10}$ of volume in cubic millimeters
● pre-1920
■ 1921-1978
▲ 1979-2016
szaibélyite
"bakerite"
1800
1825
1850
1875
1900
1925
1950
1975
2000
year of discovery


pre -1978
1979-2016 fractal
1979-2016 non-fractal
Power (1979-2016 fractal)
y = 12.08x^-0.141
R² = 0.8204
Number of minerals in a given bin
10
1
1.0E-11
1.0E-10
1.0E-09
1.0E-08
1.0E-07
1.0E-06
1.0E-05
1.0E-04
1.0E-03
1.0E-02
1.0E-01
1.0E+00
1.0E+01
1.0E+02
1.0E+03
1.0E+04
1.0E+05
1.0E+06
Size in cubic millimeters