

Article

Tellurium Minerals: Structural and Chemical Diversity and Complexity

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Abstract: The chemical diversity and complexity of tellurium minerals were analyzed using the concept of mineral systems and Shannon informational entropy. The study employed data for 176 Te mineral species known today. Tellurium minerals belong to six mineral systems in the range of one-to-six species-defining elements. For 176 tellurium minerals, only 36 chemical elements act as essential species-defining constituents. The numbers of minerals of main elements are calculated as follows (the number of mineral species is given in parentheses): O (89), H (48), Cu (48), Pb (43), Bi (31), S (29), Ag (20), Fe (20), Pd (16), Cl (13), and Zn (11). In accordance with their chemistry, all Te minerals are classified into five types of mineral systems: tellurium, oxides, tellurides and intermetalides, tellurites, and tellurates. A statistical analysis showed positive relationships between the chemical, structural, and crystallochemical complexities and the number of essential species-defining elements in a mineral. A positive statistically significant relationship between chemical and structural complexities was established. It is shown that oxygen-free and oxygen-bearing Te minerals differ sharply from each other in terms of chemical and structural complexity, with the first group of minerals being simpler than the second group. The oxygen-free Te minerals (tellurium, tellurides, and intermetallides) are formed under reducing conditions with the participation of hydrothermal solutions. The most structurally complex oxygen-bearing Te minerals originate either from chemical weathering and the oxidation of ore deposits or from volcanic exhalations (Nabokoite).

Keywords: tellurium minerals; structural complexity; chemical complexity; crystallochemical complexity; mineral systems; Shannon informational entropy

1. Introduction

Mineral ecology is a branch of mineralogy that investigates the factors that affect the distribution of minerals and the evolution of their complexity and diversity in space and time. The concept of mineral ecology appeared recently [1], although some of the ideas underlying the basic principles of this approach were formulated and discussed by Russian mineralogists [2–6]. In this paradigm, studies on the mineral evolution of individual chemical elements are of particular interest [7–16]. Among the tasks of mineral ecology is to study the distribution patterns of minerals in the Earth's crust, their diversity and complexity, and their behavior in the human environment.

The emergence of new digital technologies for big-data analysis has revolutionized this field, leading to many important discoveries in the field of structural, chemical, and genetic relationships between various minerals, and it has formulated a new research direction based on these discoveries in mineralogy [17].

Yushkin [5] justified the expediency of formulating quantitative criteria for describing the state of the mineralogical kingdom at certain stages of its development over time, and Petrov [18],

Bulkin, [19] and Yushkin [20] pointed out that the informational entropy approach can be used to measure the chemical complexity and diversity of mineralogical and geochemical systems. S. Krivovichev [21–25] proposed to use Shannon information entropy for the quantitative analysis of the structural complexities of minerals and outlined the main applications of this approach to understanding the structural evolution of minerals. It was also shown that the parameters of structural complexity are directly related to the configurational entropy of crystalline solids [26]. V. Krivovichev and Charykova [27,28] and Grew et al. [12] proposed an alternative approach based on the concept of mineral systems, which provides a useful tool for the systematization of mineral species (e.g., [27]) and allows one to order existing data into coherent structures that emphasize changes in the diversity of minerals and their composition over time. In addition, it was shown that using the concept of mineral systems, it is possible to compare different geological objects with each other in terms of their mineral diversity [29–32]. Shannon information entropy (chemical and structural complexities) and the concepts of mineral systems have also been applied to mineral evolution as a whole [33–35] and to the mineral ecology of selenium minerals, including their diversity and complexities [36–38].

The main goal of this work was to study the mineral ecology of Te minerals. The tellurium chemistry resembles that of sulfur and selenium due to the proximity of these elements in the periodic table. Similarly to S and Se, tellurium adopts four oxidation states: -2 (tellurides), 0 (native tellurium), $+4$ (tellurites), and $+6$ (tellurates). It is generally assumed that the crystal structures and reactivity of tellurium compounds can be extrapolated from S and Se. In reality, recent discoveries and well-founded observations have shown that this is not entirely true. This was shown in a special review of the fundamental concepts that are necessary to understand the unique features of Te chemistry, with an emphasis on the difference between sulfur and selenium [39]. Tellurium minerals are relatively rare, and, currently, only 176 mineral species are known [40] (Supplementary Table S1). In minerals, Te participates in various forms of intermetallic bonding in tellurides [41–43], e.g., in hessite and calaverite [44]. In O-bearing species, tellurium occurs as Te^{4+} and/or Te^{6+} cations. The geometric configuration of Te–O bonds around Te^{m+} centres form $[\text{Te}^{m+}\text{O}_n]^{m-2n}$ oxyanions [44,45]. Tetravalent Te has a stereochemically active lone pair of electrons and usually possesses an asymmetrically distorted coordination polyhedra, e.g., $[\text{Te}^{4+}\text{O}_3]^{2-}$, $[\text{Te}^{4+}\text{O}_4]^{4-}$, and $[\text{Te}^{4+}\text{O}_5]^{6-}$, sometimes with more than one coordination in the same structure [44,46]. On the contrary, Te^{6+} lacks a lone electron pair and occurs in minerals exclusively as $[\text{Te}^{6+}\text{O}_6]^{6-}$ octahedra. However, natural tellurates are stable under oxidizing conditions and, unlike selenates, do not transform into tellurites, which explains the relatively large number of tellurates in nature. The structural diversity of O-bearing Te minerals is further discussed below.

It is interesting to compare the mineral and atomic abundances in the Earth's crust for tellurium and selenium. Based on the data listed in [47], the crustal abundance by atoms for Te is less than that for Se by approximately 80 times (0.00016 and 0.013 ppm, respectively). However, the number of Te minerals exceeds that of selenium by 1.4 times (176 and 123, respectively). Thus, with a general positive trend of an increasing number of mineral species of the same element with an increase in its crustal abundance by atoms [45], tellurium differs from selenium by an anomalous mineral diversity. This difference between the atomic and mineral abundances of Te and Se is due to several reasons. Under endogenic conditions, tellurium, in contrast to selenium, is not disseminated in the sulfides and selenides and tends to form its own mineral species [41]. In addition, a certain contribution to the increase in tellurium minerals is also made by its ability to form intermetallic compounds under reducing conditions (e.g., bilibinskite, bezsmertnovite, and bogdanovite) [41].

The different behaviors of tellurium and selenium are manifested to an even greater extent by the comparison of the number of oxygen-bearing minerals (Se, 34; Te, 86) that are stable under oxidizing conditions. The latter is due to the uncommon diversity of the crystal structures of oxygen-bearing tellurium compounds [48–50], namely: the ability of Te O_n polyhedra to polymerize, forming anionic groups in the form of oligomers, chains, layers, and complex three-dimensional

2.2. Chemical, Structural and Crystallochemical Complexities

To quantify the chemical, structural and crystallochemical complexities of Te minerals, a total of pieces of 176 chemical composition data, and 117 data sets on crystal structure were reviewed. The level of structural complexity per atom ($^{str}I_G$) and per unit cell ($^{str}I_{G,total}$) [21–26] were calculated using the following equations [36]:

$$^{str}I_G = - \sum_{i=1}^k p_i \log_2 p_i \text{ (bits/atom)} \quad (1)$$

$$^{str}I_{G,total} = -v \sum_{i=1}^k p_i \log_2 p_i \text{ (bits/cell)} \quad (2)$$

where k is the number of different crystallographic orbits (Wyckoff sites) in the structure and p_i is the random choice probability for an atom from the i th crystallographic orbit, that is:

$$p_i = m_i/v \quad (3)$$

where m_i is a multiplicity of a crystallographic orbit (i.e., the number of atoms of a specific Wyckoff site in the reduced unit cell) and v is the total number of atoms in the reduced unit cell.

For several hydrated crystal structures of Te minerals, the proton positions have not been determined. In these cases, the H-correction procedure has been applied [62]. All structure complexity calculations have been performed by means of the TOPOS program package [63].

The chemical complexities of tellurium minerals were evaluated by the amount of chemical information per atom ($^{chem}I_G$) and per formula unit, f.u. ($^{chem}I_{G,total}$) [35,36]. The chemical information was calculated as follows [36]:

$$^{chem}I_G = - \sum_{i=1}^k p_i \log_2 p_i \text{ (bits/atom)} \quad (4)$$

$$^{chem}I_{G,total} = -e \sum_{i=1}^k p_i \log_2 p_i \text{ (bits/cell)} \quad (5)$$

where k is the number of species-defining chemical elements and p_i is the random choice probability for an atom of the i th element, that is:

$$p_i = c_i/e \quad (6)$$

where e is the total number of species-defining elements in the chemical formula:

$$e = \sum_{i=1}^k c_i \quad (7)$$

For the calculations of chemical complexities, the ideal chemical formulas of minerals were used (see also [27,28]).

Additionally, we calculated the crystal chemical complexities ($^{chem+str}I_G$ and $^{chem+str}I_{G,total}$) as the sum of chemical and structural complexities:

$$^{chem+str}I_G = ^{chem}I_G + ^{str}I_G \text{ (bits/atom)} \quad (8)$$

$$^{chem+str}I_{G,total} = ^{chem}I_{G,total} + ^{str}I_{G,total} \text{ (bits/f.u., cell)} \quad (9)$$

3. Results

3.1. Classification of Tellurium Minerals

Our approach allowed us to systematize mineral species by their chemical composition and to organize the available data in such a way that they complemented traditional classification schemes [61,64,65]. A certain advantage of our approach to mineral classification is its formal and unambiguous nature, although we are aware that some significant information was lost here.

As in selenium minerals classification [36], tellurium minerals are divided into five groups: native tellurium, oxides, tellurides and intermetallides, tellurites, and tellurates (anhydrous, hydrous, and with additional anions). In each of these groups, minerals can be classified by mineral systems (or the minimum number of species-forming elements). In accordance with this value, six Te mineral systems can be distinguished, with them containing from one to six species-defining elements. Native tellurium belongs to the one-component mineral system, while minerals consisting of two elements (altaite, kotulskite, hessite, etc.) belong to two-component systems, minerals containing three elements (petzite, monchetundraite, sopcheite, etc.) belong to three-component systems, etc. Our approach allowed us to distinguish the formulae of “chemically pure” minerals that contain only species-defining elements [27,28,33,34]. In this system, each mineral occupies a unique position determined by the number of species-defining elements. This also facilitates the use of digital technologies for organizing, storing, and retrieving thermodynamic data for a particular mineral [36–38]. The classification of the Te mineral systems is given in Supplementary Table S2.

3.2. Distribution of Te Minerals in Accordance with the Number of Species-Defining Elements

Tellurium minerals formed mainly in hydrothermal deposits (e.g., Bonanza Mining District, Saguache County, CO, USA [66]; Moctezuma mines, Mexico [67,68]; Alekseevskoye Mine, Sakha Republic, Russia [69]; Aginskoe deposit and Kamchatka Oblast', Russia [70,71]), the oxidation zones of ore mineral deposits (e.g., Otto Mountain, USA [49,50]; and Tombstone, AZ, USA [72]) and very rare as products of volcanic fumaroles [73]. Tellurides are also found in magmatic Cu–Ni–PGM (platinum-group-metal) sulfide deposits (e.g., Noril'sk [74] and Kola Peninsula [75] in Russia; Bushveld in South Africa [76]; and Sudbury in Canada [77]), where they have a hydrothermal origin.

Similarly to the selenium minerals [36–38], we divided tellurium minerals into two groups based on their mineral composition: oxygen-free (native tellurium, tellurium intermetallides, and tellurides; 86 minerals in total) and oxygen-bearing (tellurium oxides, tellurites, and tellurates; 89 minerals, in total). Oxygen-free tellurium minerals are quite well studied and widespread in endogenic deposits of various genetic types. In rare sulfosalts, tellurium is a crystal chemical analog of As (e.g., in goldfieldite $\text{Cu}_{10}(\text{TeS}_3)_4\text{S}$, a mineral of the tetrahedrite group; see [78,79]). In near-surface settings, tellurium (similarly to chalcophile elements) is easily oxidized, forming oxides and oxysalts when it is in an oxidation state of +4 and/or +6.

The data are given in Table 1 and Figure 2. The arithmetic mean of species-defining elements in O-free Te minerals was significantly lower ($\bar{X} = 2.8$; $\sigma_{\bar{X}} = 0.09$) than in O-bearing minerals ($\bar{X} = 4.4$; $\sigma_{\bar{X}} = 0.11$). According to Student's test, the differences in the number of species-forming elements for both groups of Te minerals were statistically significant (the confidence level is more than 99.99%)

Table 1. The mineral systems (N) of Te minerals.

N	All Minerals		O-Free		O-Bearing	
	m_i	p_i	m_i	p_i	m_i	p_i
1	1	0.6	1	1.2	-	-
2	33	18.7	31	35.6	2	2.3
3	61	34.7	42	48.3	19	21.3
4	35	29.9	8	9.2	27	30.3
5	30	17.0	5	5.7	25	28.1
6	16	9.1	-	-	16	18.0
Total	176	100.0	87	100.0	89	100.0

Note: N —the mineral systems (the number of the species-defining elements); m —number of minerals; $p_i = (m_i / \sum_{i=1}^6 m_i) \cdot 100$ probability, %.

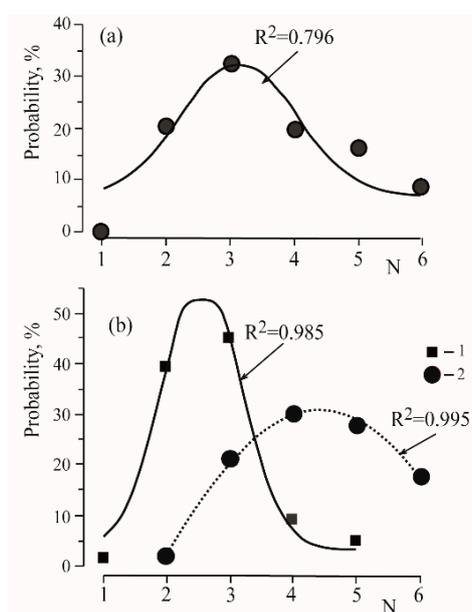


Figure 2. Distribution of Te minerals among mineral systems based on the number of the species-defining elements: (a) All minerals, (b) O-free (1, solid line), and O-bearing (2, dashed line) minerals.

The distribution of all tellurium minerals versus the mineral systems (number of species-defining elements), N , was found to be close to normal (Figure 2a). The largest number of minerals was found to consist of two and three species-defining elements (36 and 58 minerals, respectively). It is worthy to note that all minerals containing six species-defining elements were found to be O-bearing. The distributions of Te minerals between O-free and O-bearing groups depending on the number of species-defining elements, N , were also normal (Table 1 and Figure 2b). The number of species-forming elements in minerals ranged from one to six, and the maximum number of minerals was found to be formed by two and three species-forming elements.

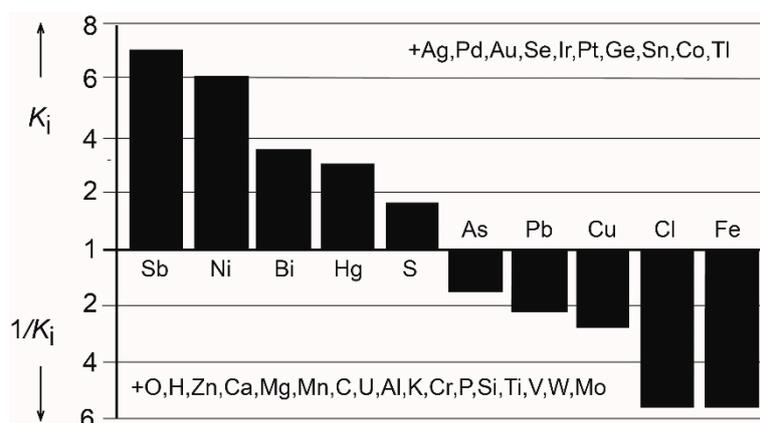
For tellurium minerals, 36 chemical elements were found to be species-defining elements. These elements were divided into three groups: (1) Elements that occur only in O-free minerals, (2) elements that occur in O-free and O-bearing minerals, and (3) elements that occur only in O-bearing tellurium minerals (Table 2).

Table 2. The species-defining elements of Te minerals separated into three groups: (1) All minerals, (2) O-free, and (3) O-bearing minerals.

Groups	Elements	All	O-Free	O-Bearing	* K_i
1	Ag	20	20	-	-
	Pd	16	16	-	-
	Au	13	13	-	-
	Se	8	8	-	-
	Ir, Pt	3	3, each	-	-
	Sn	2	2	-	-
	Co, Ge, Tl	1	1	-	-
2	Sb	8	7	1	7.00
	Ni	7	6	1	6.00
	Hg	5	4	1	4.00
	Bi	31	24	7	3.43
	S	29	18	11	1.64
	As	6	3	3	1.00
	Pb	43	14	29	0.48
	Cu	48	13	33	0.39
	Cl	13	2	11	0.18
	Fe	20	2	18	0.11
3	O	89	-	89	-
	H	48	-	48	-
	Zn	11	-	11	-
	Ca	8	-	8	-
	Mg	7	-	7	-
	Mn	6	-	6	-
	U	4	-	4	-
	C	4	-	4	-
	Al	2	-	2	-
	K	2	-	2	-
	P, Cr, Mo, Si, Ti, V, W	1	-	1, each	-

* $K_i = \text{O-free/O-bearing}$.

The difference between chemical compositions of O-free and O-bearing tellurium minerals is more clearly illustrated by the diagram shown in Figure 3.

**Figure 3.** The species-defining elements (N) of three groups of Te minerals and the concentration coefficient $K_i = \text{O-free/O-bearing}$ (see Table 2).

3.3. Chemical, Structural and Crystallochemical Complexities of Tellurium Minerals

According to Equations (1)–(9), the complexity indicators of tellurium minerals belonging to different mineral systems (or the number (N) of different species-defining chemical elements) were calculated. The average chemical, structural, and crystal–chemical complexities of minerals and associated statistical parameters are shown in Table 3 and Figure 4. The dependencies of different complexities from N were approximated by the following functions (the corresponding curves are plotted in Figure 3):

$$I_G^{\text{chem}} = 1.900 - 3.743 \times \exp(-N/1.472) \quad (R^2 = 0.997) \quad (10)$$

$$I_G^{\text{str}} = 3.580 - 7.239 \times \exp(-N/1.397) \quad (R^2 = 0.979) \quad (11)$$

$$I_{G,\text{total}}^{\text{chem}} = 1.622 \times \exp(N/1.459) \quad (R^2 = 0.999) \quad (12)$$

$$I_{G,\text{total}}^{\text{str}} = -54.512 + 53.873 \times N \quad (R^2 = 0.985) \quad (13)$$

$$I_G^{\text{chem+str}} = 5.520 - 11.089 \times \exp(-N/1.396) \quad (R^2 = 0.979) \quad (14)$$

$$I_{G,\text{total}}^{\text{chem+str}} = -80.254 + 69.784 \times N \quad (R^2 = 0.980) \quad (15)$$

Table 3. Chemical, structural, and crystallochemical (chem + str) complexities of tellurium minerals according to the number of species-defining chemical elements (N) *.

N	m	chem I_G				m_i	str I_G				chem+str I_G			
		[bits/atom]		[bits/f.u.]			[bits/atom]		[bits/cell]		[bits/atom]		[bits/f.u.cell]	
		\bar{X}	σ_X^-	\bar{X}	σ_X^-		\bar{X}	σ_X^-	\bar{X}	σ_X^-	\bar{X}	σ_X^-	\bar{X}	σ_X^-
1	1	0			0	29	1	0			0			
2	36	0.96	0.02	7.0	1.67	29	2.07	0.24	72.1	25.9	3.3	0.3	82.0	27.9
3	58	1.38	0.02	12.8	1.17	37	2.44	0.16	81.2	13.3	3.8	0.1	94.9	13.9
4	35	1.63	0.03	26.2	2.68	18	3.10	0.21	168.3	34.1	4.7	0.2	190.4	35.4
5	29	1.79	0.03	50.1	6.62	21	3.57	0.18	199.4	36.4	5.3	0.2	245.2	41.6
6	16	1.90	0.04	101.8	18.77	11	3.58	0.22	283.3	41.2	5.5	0.2	371.5	39.4

* m_i = number of minerals taken into account; \bar{X} = arithmetic mean; σ_X^- = standard error of arithmetic mean.

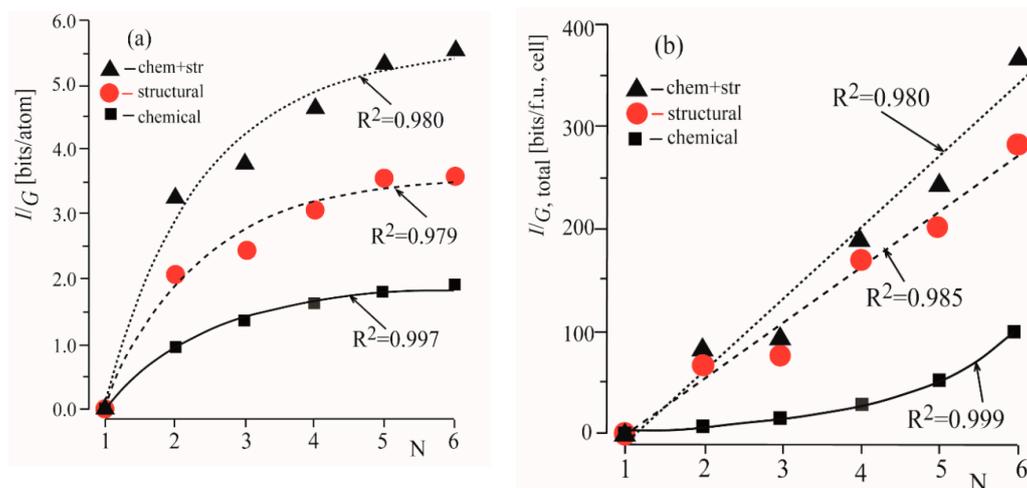


Figure 4. Dependence of chemical, structural, and crystal–chemical complexities of tellurium minerals on the number of species-defining chemical elements (N). The complexity per atom (a) and per unit cell or per formula unit (b).

The obtained data indicated the presence of a statistically significant (a confidence level of more than 99%) and positive relationship between the chemical, structural, and crystallochemical (chemical + structural) complexities of tellurium minerals and the number of species-defining chemical elements in their mineral formula.

To compare the complexity of tellurium minerals formed in various geochemical environments, they were divided into two groups: (1) oxygen-free minerals (tellurides and native tellurium) formed in endogenous conditions and (2) oxygen-bearing (oxides and oxysalts) formed in exogenous conditions as a result of chemical weathering and fumarolic activity. A statistical analysis showed (Table 4) that the average arithmetic values of structural, chemical, and crystallochemical complexities for O-free tellurium minerals are significantly lower than for O-bearing species. The Student's test [80] showed that the differences are statistically significant (see Table 4).

Table 4. Chemical, structural, and crystallochemical complexities of two groups (O-free and O-bearing) tellurium minerals *.

Complexities	O-free			O-bearing			Student's <i>t</i> -test	
	m_i	\bar{X}	$\sigma_{\bar{X}}$	m_i	\bar{X}	$\sigma_{\bar{X}}$	<i>t</i>	<i>p</i>
chem I_G [bits/atom]	87	1.28	0.05	89	1.62	0.03	−6.92	<0.0001
str I_G [bits/atom]	56	2.19	0.16	63	3.20	0.12	−5.10	<0.0001
chem $I_{G,total}$ [bits/f.u.]	87	11.4	1.1	89	45.9	5.2	−6.38	<0.0001
str $I_{G,total}$ [bits/cell]	56	69.3	15.6	63	183.9	18.5	−4.65	<0.0001
chem+str I_G [bits/atom]	56	3.69	0.20	63	4.82	0.14	−4.71	<0.0001
chem+str $I_{G,total}$ [bits/f.u.,cell]	56	81.2	16.6	63	223.8	21.1	−5.19	<0.0001

* m_i = number of minerals taken into account; \bar{X} = arithmetic mean; $\sigma_{\bar{X}}$ = standard error of arithmetic mean; *p*—probability value or *p*-value.

4. Conclusions

The obtained statistical correlations between the complexities (chem, str, and str + chem) of tellurium minerals showed that the minerals become more complex during the chemical weathering of primary ores. These indicators regularly and statistically significantly increase from the endogenic to exogenic associations, and they reflect the character and direction of mineral matter's variations in the evolution of mineral systems and can be used when analyzing their evolutionary patterns. This is in good agreement with the general trend of chemical differentiation of matter with the evolution of the Earth, which was pointed out in [1–5], where general patterns in the evolution of mineral species on Earth were established, including the complexity of the composition, structure, and diversity of minerals over geological time. In our case, this trend manifested itself as a complexity of later mineral assemblages compared to the primary ones. In addition, the average number of chemical elements in a mineral increases from primary to secondary minerals, which is consistent with the results of the information considerations presented here. On the example of selenium minerals [36], it was shown that the change in the complexity of minerals follows the same trend: more complex minerals occur over time, and simple ones are replaced. This trend of O-bearing minerals being more complex now seems an empirical rule that applies for many elements. That was found also for cobalt minerals [13].

Current work has shown that this conclusion is also true for the minerals of other elements, since the increase in their complexity over time reflects the general trend in the evolution of natural matter. Chemical differentiation leads to an increase in the complexity and diversity of tellurium minerals, which favor the formation of local concentrations of some rare elements and the creation of new geochemical environments.

In conclusion, let us note that our approach makes it possible to move from comparing the tellurium minerals of primary and secondary genesis from a qualitative to a quantitative basis. This gives a more vivid representation of the studied objects and can also reveal the ability of individual chemical elements to form their own mineral species.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/7/623/s1>, Table S1: Tellurium minerals: Number of species-defining's elements (*N*) chemical formula, and number of localities (NL); Table S2: Classification of mineral systems of tellurium minerals according to number of species-defining elements (*N*) an chemical composition.

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References

1. Hazen, R.M.; Grew, E.S.; Downs, R.T.; Golden, J.; Hystad, G. Mineral ecology: Chance and necessity in the mineral diversity of terrestrial planets. *Can. Mineral.* **2015**, *53*, 295–324. [[CrossRef](#)]
2. Zhabin, A.G. Is there evolution of mineral species on Earth? *Dokl. Akad. Nauk SSSR* **1979**, *247*, 199–202.
3. Zhabin, A.G. Problems of the mineral phylogeny. In *New Ideas in Genetic Mineralogy*; Nauka: Leningrad, Russia, 1983; pp. 7–12. (In Russian)
4. Yushkin, N.P. Evolutionary ideas in modern mineralogy. *Zap. Vsesoyuznogo Mineral. Obs.* **1982**, *111*, 432–442. (In Russian)
5. Yushkin, N.P. (Ed.) *Minerals, Mineral Formation, Structure, Diversity and Evolution of the Mineral World, the Role of Minerals in the Origin of Life, Biomineral Interactions*; Intitute of Geology of Komi Science Centre RAS: Syktyvkar, Russia, 2008; pp. 455–459. (In Russian)
6. Krivovichev, S.V. Complexity, diversity and evolution of the mineral world: From Vernadsky to the present day. In *Vernadsky and XXI Century: Geosphere, Biosphere, Noosphere and Symmetry*; St. Ivan Rilski: Sofia, Bulgaria, 2013; pp. 26–32. (In Russian)
7. Hazen, R.M.; Ewing, R.C.; Sverjensky, D.A. Evolution of uranium and thorium minerals. *Am. Mineral.* **2009**, *94*, 1293–1311. [[CrossRef](#)]
8. Hazen, R.M.; Golden, J.; Downs, R.T.; Hystad, G.; Grew, E.S.; Azzolini, D.; Sverjensky, D.A. Mercury (Hg) mineral evolution: A mineralogical record of supercontinental assembly, changing ocean geochemistry, and the emerging terrestrial biosphere. *Am. Mineral.* **2012**, *97*, 1013–1042. [[CrossRef](#)]
9. Hazen, R.M.; Hummer, D.R.; Hystad, G.; Downs, R.T.; Golden, J.J. Carbon mineral ecology: Predicting the undiscovered minerals of carbon. *Am. Mineral.* **2016**, *101*, 889–906. [[CrossRef](#)]
10. Grew, E.S.; Hazen, R.M. Beryllium mineral evolution. *Am. Mineral.* **2014**, *99*, 999–1021. [[CrossRef](#)]
11. Grew, E.S.; Hystad, G.; Hazen, R.M.; Krivovichev, S.V.; Gorelova, L.A. How many boron minerals occur in Earth's upper crust? *Am. Mineral.* **2017**, *102*, 1573–1587. [[CrossRef](#)]
12. Grew, E.S.; Krivovichev, S.V.; Hazen, R.M.; Hystad, G. Evolution of structural complexity in boron minerals. *Can. Mineral.* **2016**, *54*, 125–143. [[CrossRef](#)]
13. Hazen, R.M.; Hystad, G.; Golden, J.J.; Hummer, D.R.; Liu, C.; Downs, R.T.; Morrison, S.M.; Grew, E.S. Cobalt mineral ecology. *Am. Mineral.* **2017**, *102*, 108–116. [[CrossRef](#)]
14. Liu, C.; Hystad, G.; Golden, J.J.; Hummer, D.R.; Downs, R.T.; Morrison, S.M.; Ralph, J.P.; Hazen, R.M. Chromium mineral ecology. *Am. Mineral.* **2017**, *102*, 612–619. [[CrossRef](#)]
15. Liu, C.; Eleish, A.; Hystad, G.; Golden, J.J.; Downs, R.T.; Morrison, S.M.; Hummer, D.R.; Ralph, J.P.; Fox, P.; Hazen, R.M. Analysis and visualization of vanadium mineral diversity and distribution. *Am. Mineral.* **2018**, *103*, 1080–1086. [[CrossRef](#)]
16. Grew, E.S.; Hystad, G.; Toapanta, M.P.; Eleish, A.; Ostroverkhova, A.; Golden, J.; Hazen, R.M. Lithium mineral evolution and ecology: Comparison with boron and beryllium. *Eur. J. Mineral.* **2019**, *31*, 755–774. [[CrossRef](#)]
17. Hazen, R.M.; Downs, R.T.; Eleish, A.; Fox, P.; Gagné, O.C.; Golden, J.J.; Grew, E.S.; Hummer, D.R.; Hystad, G.; Krivovichev, S.V.; et al. Data-Driven Discovery in Mineralogy: Recent Advances in Data Resources, Analysis, and Visualization. *Engineering* **2019**, *5*, 397–405. [[CrossRef](#)]
18. Petrov, T.G. On the measure of complexity of geochemical systems from the viewpoint of information theory. *Dokl. Akad. Nauk SSSR* **1970**, *191*, 924–926. (In Russian)

19. Bulkin, G.A. Complexity of geochemical systems and their equilibrium. *Dokl. Akad. Nauk SSSR* **1972**, *204*, 956–959. (In Russian)
20. Yushkin, N.P. *Theory and Methods of Mineralogy*; Nauka: Leningrad, Russia, 1977. (In Russian)
21. Krivovichev, S.V. Topological complexity of crystal structures: Quantitative approach. *Acta Crystallogr.* **2012**, *68*, 393–398. [[CrossRef](#)]
22. Krivovichev, S.V. Structural complexity of minerals: Information storage and processing in the mineral world. *Mineral. Mag.* **2013**, *77*, 275–326. [[CrossRef](#)]
23. Krivovichev, S.V. Which inorganic structures are the most complex? *Angew. Chem. Int. Ed.* **2014**, *53*, 654–661. [[CrossRef](#)]
24. Krivovichev, S.V. Structural complexity of minerals and mineral parageneses: Information and its evolution in the mineral world. In *Highlights in Mineralogical Crystallography*; Danisi, R., Armbruster, T., Eds.; Walter de Gruyter GmbH: Berlin, Germany; Boston, MA, USA, 2015; pp. 31–73.
25. Krivovichev, S.V. Ladders of information: What contributes to the structural complexity in inorganic crystals. *Z. Krist.-Cryst. Mater.* **2018**, *233*, 155–161. [[CrossRef](#)]
26. Krivovichev, S.V. Structural complexity and configurational entropy of crystalline solids. *Acta Crystallogr.* **2016**, *72*, 274–276.
27. Krivovichev, V.G.; Charykova, M.V. *Classification of Mineral Systems*; St. Petersburg University Press: Saint Petersburg, Russia, 2013; 196p. (In Russian)
28. Krivovichev, V.G.; Charykova, M.V. Number of Minerals of Various Chemical elements: Statistics 2012 (a New Approach to an Old Problem). *Zap. Ross. Mineral. Obs.* **2013**, *142*, 36–42, (In Russian; English translation: *Geol. Ore Depos.* **2014**, *56*, 553–559). [[CrossRef](#)]
29. Krivovichev, V.G.; Charykova, M.V. Mineral Systems, Their Types, and Distribution in Nature. I.; Khibiny, Lovozero, and the Mont Saint-Hilaire. *Zap. Ross. Mineral. Obs.* **2015**, *144*, 1–12, (In Russian; English translation: *Geol. Ore Depos.* **2016**, *58*, 551–558). [[CrossRef](#)]
30. Krivovichev, V.G.; Charykova, M.V. Mineral and Physicochemical Systems of Evaporites: Geochemical and Thermodynamic Aspects. *Zap. Ross. Mineral. Obs.* **2016**, *145*, 30–43, (In Russian; English translation: *Geol. Ore Depos.* **2017**, *59*, 575–583). [[CrossRef](#)]
31. Krivovichev, V.G.; Charykova, M.V. Mineral Systems, Their Types, and Distribution in Nature: 2. Products of Contemporary Fumarole Activity at Tolbachik Volcano (Russia) and Vulcano (Italy). *Zap. Ross. Mineral. Obs.* **2017**, *146*, 15–28, (In Russian; English translation: *Geol. Ore Depos.* **2017**, *59*, 677–686). [[CrossRef](#)]
32. Krivovichev, V.G.; Charykova, M.V. Mineral Systems, Their Types, and Distribution in Nature: 3. Otto Mountain (USA) and Dragon (Bolivia) Deposits. *Zap. Ross. Mineral. Obs.* **2018**, *147*, 14–27, (In Russian; English translation: *Geol. Ore Depos.* **2019**, *61*, 589–597). [[CrossRef](#)]
33. Krivovichev, V.G.; Charykova, M.V.; Krivovichev, S.V. The concept of mineral systems and its application to the study of mineral diversity and evolution. *Eur. J. Mineral.* **2018**, *30*, 219–230. [[CrossRef](#)]
34. Krivovichev, V.G.; Charykova, M.V.; Krivovichev, S.V. Mineral systems based on the number of species-defining chemical elements in minerals: Their diversity, complexity, distribution and mineral evolution of Earth's crust—A review. *Zap. Ross. Mineral. Obs.* **2020**, *149*, 1–22. (In Russian)
35. Krivovichev, S.V.; Krivovichev, V.G.; Hazen, R.M. Structural and chemical complexity of minerals: Correlations and time evolution. *Eur. J. Mineral.* **2018**, *30*, 231–236. [[CrossRef](#)]
36. Krivovichev, V.G.; Krivovichev, S.V.; Charykova, M.V. Selenium Minerals: Structural and Chemical Diversity and Complexity. *Minerals* **2019**, *9*, 455. [[CrossRef](#)]
37. Charykova, M.V.; Krivovichev, V.G. Mineral systems and the thermodynamics of selenites and selenates in the oxidation zone of sulfide ores—A review. *Mineral. Petrol.* **2017**, *111*, 121–134. [[CrossRef](#)]
38. Krivovichev, V.G.; Charykova, M.V.; Vishnevsky, A.V. The thermodynamics of selenium minerals in near-surface environments. *Minerals* **2017**, *7*, 188. [[CrossRef](#)]
39. Chivers, T.; Laitinen, R. Tellurium: A maverick among the chalcogens. *Chem. Soc. Rev.* **2015**, *44*, 1725–1739. [[CrossRef](#)] [[PubMed](#)]
40. Pasero, M. The New IMA List of Minerals. 2020. Available online: <http://ima-cnmc.nrm.se/imalist.htm> (accessed on 15 March 2020).
41. Ivanov, V.V.; Yushko-Zakharova, O.E. *Tellurium, Geologicheskii Spravochnik po Siderofil'nym i Khalkofil'nym Elementam*; (Geological Reference Book of Chalcophile and Siderophile Elements); Nedra: Moscow, Russia, 1989; pp. 353–424. (In Russian)

42. Bindi, L.; Biagioni, C. A crystallographic excursion in the extraordinary world of minerals: The case of Cu- and Ag-rich sulfosalts. *Acta Crystallogr.* **2018**, *74*, 527–538. [[CrossRef](#)]
43. Helmy, H.M.; Ballhaus, C.; Berndt, J.; Bockrath, C. Wohlgemuth-Ueberwasser, C. Formation of Pt, Pd and Ni tellurides: Experiments in sulfide–telluride systems. *Contrib. Mineral. Petrol.* **2007**, *153*, 577–591. [[CrossRef](#)]
44. Missen, O.P.; Rama, R.; Mills, S.J.; Etschmanna, B.; Reith, F.; Shuster, J.; Smithe, D.J.; Bruggera, J. Love is in the Earth: A review of tellurium (bio)geochemistry in surface environments. *Earth-Sci. Rev.* **2020**, *204*, 103150. [[CrossRef](#)]
45. Christy, A.G.; Mills, S.J.; Kampf, A.R.; Housley, R.M.; Thorne, B.; Marty, J. The relationship between mineral composition, crystal structure and paragenetic sequence: The case of secondary Te mineralization at the Bird Nest drift, Otto Mountain, California, USA. *Mineral. Mag.* **2016**, *80*, 291–310. [[CrossRef](#)]
46. Mills, S.J.; Christy, A.G. Revised values of the bond-valence parameters for $\text{Te}^{\text{IV}}\text{-O}$, $\text{Te}^{\text{VI}}\text{-O}$ and $\text{Te}^{\text{IV}}\text{-Cl}$. *Acta Crystallogr. Sect. B* **2013**, *69*, 145–149. [[CrossRef](#)]
47. Christy, A.G. Anomalous mineralogical diversity in the Periodic Table, and its causes. *Mineral. Mag.* **2015**, *79*, 33–49. [[CrossRef](#)]
48. Housley, R.M.; Kampf, A.R.; Mills, S.J.; Marty, J.; Thorne, B. The remarkable occurrence of rare secondary minerals at Otto Mountain near Baker, California—Including seven new species. *Rocks. Miner.* **2011**, *86*, 132–142. [[CrossRef](#)]
49. Christy, A.G.; Mills, S.J.; Kampf, A.R. A review of the structural architecture of tellurium oxycompounds. *Mineral. Mag.* **2016**, *80*, 415–545. [[CrossRef](#)]
50. Hazen, R.M.; Hystad, G.; Downs, R.T.; Golden, J.J.; Pires, A.J.; Grew, E.S. Earth’s “missing” minerals. *Am. Mineral.* **2015**, *100*, 2344–2347. [[CrossRef](#)]
51. Christy, A.G.; Mills, S.J. Effect of lone-pair stereoactivity on polyhedral volume and structural flexibility: Application to TeIVO_6 octahedra. *Acta Crystallogr. Sect. B* **2013**, *69*, 446–456.
52. Krivovichev, V.G.; Charykova, M.V. *Termodinamika Mineral’nykh Ravnovesii v Sistemakh s Toksichnymi Komponentami. I. Selen;* (Thermodynamics of Mineral Equilibria in Systems with Toxic Components. I. Selenium); St. Petersburg University Press: Saint Petersburg, Russia, 2006; 132p. (In Russian)
53. Huheey, J.E. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper & Row: New York, NY, USA, 1983; 936p.
54. Korolkov, D.V.; Skorobogatov, G.A. *Theoretical Chemistry*; St. Petersburg University Press: Saint Petersburg, Russia, 2004; 655p. (In Russian)
55. Mandarino, J.A.; Nickel, E.H.; Cesbron, F. Rules of procedure of the Commission on New Minerals and Mineral Names, International Mineralogical Association. *Can. Mineral.* **1984**, *22*, 367–368. [[CrossRef](#)]
56. Nickel, E.H. The definition of a mineral. *Can. Miner.* **1995**, *33*, 689–690.
57. Nickel, E.H.; Grice, J.D. The IMA Commission on New Minerals and Mineral Names: Procedures and Guidelines on Mineral Nomenclature. *Can. Miner.* **1998**, *36*, 91–926.
58. Nickel, E.H.; Mandarino, J.A. Procedures involving the IMA Commission on New Minerals and Mineral Names and guidelines on mineral nomenclature. *Am. Miner.* **1987**, *72*, 1031–1042. [[CrossRef](#)]
59. Hawthorne, F.C. The use of end-member charge-arrangements in defining new mineral species and heterovalent substitutions in complex minerals. *Can. Mineral.* **2002**, *40*, 699–710. [[CrossRef](#)]
60. Hatert, F.; Burke, E.A.J. The IMA-CNMNC dominant-constituent rule revised and extended. *Can. Mineral.* **2008**, *46*, 717–728. [[CrossRef](#)]
61. Bulakh, A.G.; Zolotarev, A.A.; Krivovichev, V.G. *Structures, Isomorphism, Formulae, Classification of Minerals*; St. Petersburg University Press: Saint Petersburg, Russia, 2014; 133p. (In Russian)
62. Pankova, Y.A.; Gorelova, L.A.; Krivovichev, S.V.; Pekov, I.V. The crystal structure of ginorite, $\text{Ca}_2[\text{B}_{14}\text{O}_{20}(\text{OH})_6](\text{H}_2\text{O})_5$, and the analysis of dimensional reduction and structural complexity in the $\text{CaO-B}_2\text{O}_3\text{-H}_2\text{O}$ system. *Eur. J. Mineral.* **2018**, *30*, 277–287. [[CrossRef](#)]
63. Blatov, V.A.; Shevchenko, A.P.; Proserpio, D.M. Applied topological analysis of crystal structures with the program package ToposPro. *Cryst. Growth Des.* **2014**, *14*, 3576–3586. [[CrossRef](#)]
64. Mills, S.J.; Hatert, F.; Nickel, E.H.; Ferraris, G. The standardisation of mineral group hierarchies: Application to recent nomenclature proposals. *Eur. J. Mineral.* **2009**, *21*, 1073–1080. [[CrossRef](#)]
65. Strunz, H.; Nickel, E.H. *Strunz Mineralogical Tables*, 9th ed.; Schweizerbart’sche Verlagsbuchhandlung: Berlin/Stuttgart, Germany, 2001; 870p.

66. Bindi, L.; Cipriani, C. Mazzettiite, $\text{Ag}_3\text{HgPbSbTe}_5$, a new mineral species from Findley Gulch, Saguache County, Colorado, USA. *Can. Mineral.* **2004**, *42*, 1739–1743. [[CrossRef](#)]
67. Stanley, C.J.; Criddle, A.J.; Chisholm, J.E. Benleonardite, a new mineral from the Bambolla mine, Moctezuma, Sonora, Mexico. *Mineral. Mag.* **1986**, *50*, 681–686. [[CrossRef](#)]
68. Williams, S.A. Cuztite and eztlite, two new tellurium minerals from Moctezuma, Mexico. *Mineral. Mag.* **1982**, *46*, 257–259. [[CrossRef](#)]
69. Lipovetskii, A.G.; Borodaev, Y.S.; Zav'yalov, E.N. Aleksite, $\text{PbBi}_2\text{Te}_2\text{S}_2$, a new mineral. *Zap. Vsesoyuznogo Mineral. Obs.* **1978**, *107*, 315–321. (In Russian)
70. Spiridonov, E.M.; Chvileva, T.N. Bezsmertnovite $\text{Au}_4\text{Cu}(\text{Te,Pb})$; a new mineral from the zone of oxidation of deposits of the Far East. *Dokl. Akad. Nauk SSSR* **1979**, *249*, 185–189. (In Russian)
71. Spiridonov, E.M.; Bezsmertnaya, M.S.; Chileva, T.N.; Bezsmertny, V.V. Bilibinskite, $\text{Au}_3\text{Cu}_2\text{PbTe}_2$, a new mineral of gold-telluride deposits. *Zap. Vsesoyuznogo Mineral. Obs.* **1978**, *107*, 310–315. (In Russian) [[CrossRef](#)]
72. Tait, K.T.; Dicecco, V.; Ball, N.A.; Hawthorne, F.C.; Kampf, A.R. Backite, $\text{Pb}_2\text{Al}(\text{TeO}_6)\text{Cl}$, a new tellurate mineral from the Grand Central mine, Tombstone Hills, Cochise County, Arizona: Description and crystal structure. *Can. Mineral.* **2015**, *52*, 935–942. [[CrossRef](#)]
73. Popova, V.I.; Popov, V.A.; Rudashevskiy, N.S.; Glavatskikh, S.F.; Polyakov, V.O.; Bushmakin, A.F. Nabokoite $\text{Cu}_7\text{TeO}_4(\text{SO}_4)_5\cdot\text{KCl}$ and atlasovite $\text{Cu}_6\text{Fe}^{3+}\text{Bi}^{3+}\text{O}_4(\text{SO}_4)_5\cdot\text{KCl}$. New minerals of volcanic exhalations. *Zap. Vsesoyuznogo Mineral. Obs.* **1987**, *116*, 358–367.
74. Kovalenker, V.A.; Begizov, V.D.; Evstigneeva, T.L.; Troneva, N.V.; Ryabikin, V.A. Maslovite, PtBiTe : A new mineral from the October copper-nickel deposit. *Geol. Rudn. Mestorozhdenii* **1979**, *21*, 94–104. (In Russian)
75. Subbotin, V.V.; Vymazalová, A.; Laufek, F.; Savchenko, Y.E.; Stanley, C.J.; Gabov, D.A.; Plášil, J. Mitrofanovite, Pt_3Te_4 , a new mineral from the East Chuarvy deposit, Fedorovo-Pana intrusion, Kola Peninsula, Russia. *Mineral. Mag.* **2019**, *83*, 523–530. [[CrossRef](#)]
76. Kingston, G.A. The occurrence of platinoid bismuthotellurides in the Merensky Reef at Rustenburg platinum mine in the western Bushveld. *Mineral. Mag.* **1966**, *35*, 815–834. [[CrossRef](#)]
77. Hawley, J.E.; Berry, L.G. Michenerite and froodite, palladium bismuthide minerals [Ontario]. *Can. Mineral.* **1958**, *6*, 200–209.
78. Kalbskopf, R. Synthese und kristallstruktur von $\text{Cu}_{12-x}\text{Te}_4\text{S}_{13}$, dem tellur-endglied der fahlerze. *Tscherm. Miner. Petrogr. Mitt.* **1974**, *21*, 1–10. (In German) [[CrossRef](#)]
79. Makovicky, E.; Karup-Moller, S. Exploratory studies of substitutions in the tetrahedrite/tennantite—Goldfieldite solid solution. *Can. Mineral.* **2017**, *55*, 233–244. [[CrossRef](#)]
80. Wall, F.J. *Statistical Data Analysis Handbook*; McGraw-Hill Inc.: New York, NY, USA, 1986; 546p.

