

Periodicity in Variation of Thermodynamic, Physical, and Biogeochemical Properties of Elements

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The heat capacity and entropy of elementary substances are considered in this work as a thermodynamic basis of geochemical systematics of the respective elements. According to the Oddo–Harkins rule, they are divided into even and odd groupings based on their abundance. In order to justify this division, the mean composition of carbonaceous chondrites (C) that makes up only 2–5% of the total chondrite dips [2] has been used in [1]. The predominant ordinary chondrites are divided into approximately equal low-Fe (L) and high-Fe (H) varieties. This subdivision reflects a bimodality of the dominating group of meteorites [3]. The abundance of chemical elements in the mean composition of the ordinary H-chondrites [4] is shown in Fig. 1. The even elements occupy the maximum positions at extremes of various orders, whereas the odd elements occupy the minimum positions as is shown by dashed thin lines. This subdivision fits the Oddo–Harkins rule, but the latter does not work in the region with low ordinal element numbers. For example, the even element Be is characterized by a lower abundance than the odd Li and B. Similarly, the total cosmic abundance of the odd element H is much higher than the abundance of the even He. This specific feature of light elements (H, He, Li, Be, and B) is caused by their special origin, as will be considered hereafter.

An anomalous characteristic of the light elements is also reflected in the thermodynamic and physical properties of the respective elementary substances presented in the general system of elements (Table 1) based on their standard heat capacity and entropy. These parameters have been calculated for 1 g of the material based on their gram-atomic (or molecular) weights published in [5]. The melting temperature (sublimation temperature for C, P, and As) is also included in this table as a physical characteristic of elementary substances. This parameter most closely corre-

lates with thermodynamic properties of elements and indicates the stability of their crystalline state.

We used the standard values of heat capacity and entropy (C_{p298}° and S_{298}°) of substances that occur in the gaseous or condensed state at the respective parameters ($P = 1$ bar; $T = 298$ K). Light halogens (Cl, F), hydrogen, noble gases, nitrogen, and oxygen are gaseous substances that differ from the solid substances by having higher entropy. As in [1], the even and odd elements are considered separately, in agreement with their principal difference in abundance. The chemical elements are considered in terms of the heat capacity and entropy of the respective elementary substances with indication of their melting temperature (Figs. 2, 3). In fact, these parameters control the periodic entropic systems of odd (Fig. 2) and even (Fig. 3) chemical elements. Alternation of entropy minimums and maximums in these systems clearly correlates with a periodicity in variation of physical properties of substances. The most refractory elements are related to the minimums of entropy, while the fusible elements are confined to the maximums. Only insignificant deviations from this general relationship are known. For example, uranium has a lower melting temperature (1403 K) than thorium (2028 K) which has a higher entropy. Similarly, the sublimation temperature of phosphorus (702 K) which has a higher than the melting temperature of aluminum (993 K) at lower entropy. Anomalous relationships between entropy and melting temperature are also characteristic of molybdenum (2893 K) and ruthenium (2523 K). These departures are likely related to polymorphous transformations of the substances that markedly change their entropy, as is exemplified in Fig. 3 for diamond and graphite.

The diagrams considered make up the thermodynamic basis of the periodic system of chemical elements. Fragments of this system are arranged in Table 2 separately for odd (Fig. 2) and even (Fig. 3) elements. The zero groups include elements with the highest entropy (halogens and noble gases). They are crowned by hydrogen and helium, which have the highest entropy and heat capacity (Table 1). Periods of the light element (H–Li–B–N and He–Be–C–O) start from this point. In contrast to all other periods characterized by monotonously decreasing entropy and an increase of

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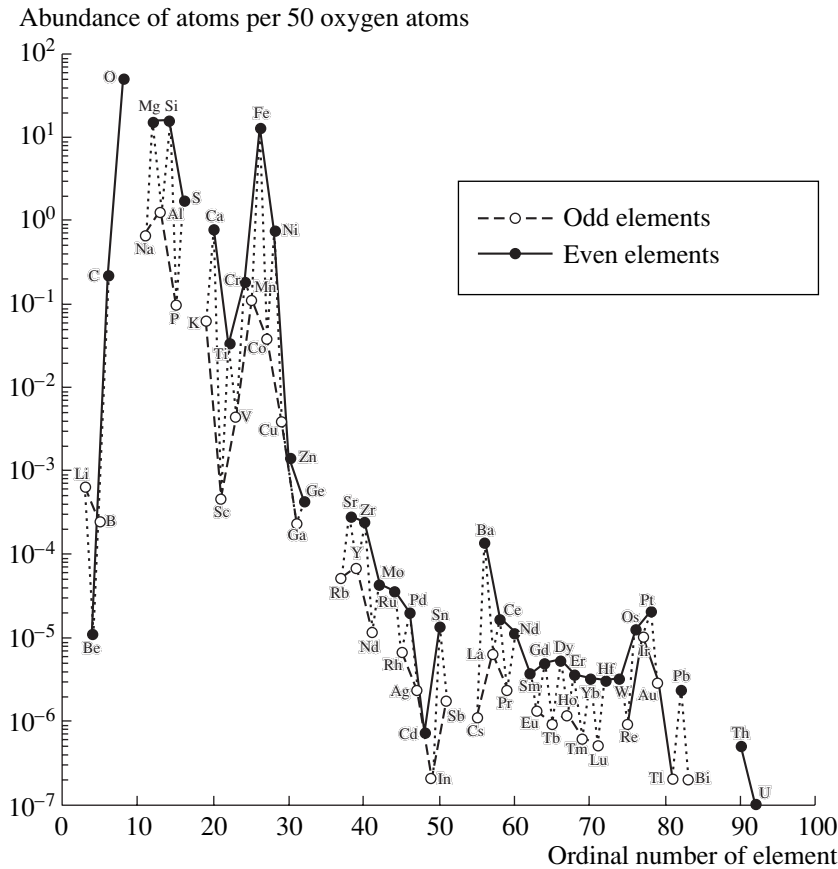


Fig. 1. Abundances of chemical elements in the average composition of ordinary H-chondrites [4].

ordinal element numbers, the light element periods are anomalies, with minimal entropy and maximal melting temperature found at boron and carbon. The anomalous features of light elements are also expressed in their discrepancy with respect to entropy trends of the group (I–IV). These elements are shifted to the region with a lower entropy by dashed arrows (Al → B, Mg → Be, and Si → C) in Figs. 2 and 3 as denoted. They reflect an anomalous deepening of entropy minima that fall on the light elements of the hydrogen and helium periods.

The anomalous thermodynamic properties of chemical elements related to the hydrogen and helium periods reflect their specific origin. They were formed together with hydrogen and helium in the prestellar period of the evolution of the Universe as a result of the Big Bang. The formation of heavier elements occurred during stellar evolution. According to the commonly accepted models, the lightest Li, Be, and B elements are prestellar. However, carbon, with its anomalous minimum entropy increasing during the phase transition from graphite to diamond, is also unequivocally related to the thermodynamically anomalous elements. The compaction of this mineral and ordering of its structure correlate with a substantial decrease in its entropy. Consequently, diamond has an extremely low entropy minimum incommensurable with the entropy minimum of

graphite, which is also anomalous, but to a lesser extent. In the periodic system of elements, carbon is included in the same group as Ge and Si. Hence, according to the entropic position, carbon should be placed on the line connecting these elements and extending toward the region with a higher heat capacity ($C_{p298}^{\circ} = 0.814$, $S_{p298}^{\circ} = 0.723 \text{ J g}^{-1} \text{ K}^{-1}$). The successive transition from carbon to graphite ($C_{p298}^{\circ} = 0.509$, $S_{p298}^{\circ} = 0.478 \text{ J g}^{-1} \text{ K}^{-1}$) and diamond ($C_{p298}^{\circ} = 0.509$, $S_{p298}^{\circ} = 0.197 \text{ J g}^{-1} \text{ K}^{-1}$) is accompanied by an appreciable decrease of entropy and respective stabilization of their crystalline states. The stabilization promoted a very high sublimation temperature of graphite and diamond (3773 K) and an anomalously low entropic position on the diagram (Fig. 3). The graphite–diamond transition clearly shows the indicative role of entropy. Its decrease during the formation of dense variations of elementary substances demonstrates their stabilization and broadens the possibility of the formation of metastable substances. The entropy minima correlate with element abundance maxima. For example, a deep entropy minimum falling on La (Fig. 2) corresponds to its maximal abundance in the series of odd chemical elements (Fig. 1). Figures 2 and 3 demon-

Table 1. Specific heat capacity, entropy ($\text{J} \cdot \text{g}^{-1} \text{K}^{-1}$), and melting temperature (K) of elementary substances

Element	$C_{p, 298}^{\circ}$	S_{298}°	T	Element	$C_{p, 298}^{\circ}$	S_{298}°	T	Element	$C_{p, 298}^{\circ}$	S_{298}°	T			
1	H	14.3	64.7	14	35	Br	0.474	0.952	266	69	Tm	0.160	0.423	1818
2	He	5.20	31.5	1.75	36	Kr	0.248	1.957	116	70	Yb	0.145	0.363	1097
3	Li	3.57	4.20	454	37	Rb	0.360	0.886	313	71	Lu	0.154	0.282	1936
4	Be	1.82	1.06	1560	38	Sr	0.310	0.606	1041	72	Hf	0.144	0.244	2500
5	B	1.03	5.42	2300	39	Y	0.282	0.517	1799	73	Ta	0.140	0.229	3287
6	C	0.710	4.78	3773	40	Zr	0.278	0.428	2125	74	W	0.132	0.178	3680
7	N	1.03	6.81	63	41	Nb	0.265	0.394	2740	75	Re	0.135	0.196	3453
8	O	0.918	6.41	54	42	Mo	0.249	0.299	2890	76	Os	0.123	0.171	3300
9	F	0.824	5.33	54	43	Tc	0.246	0.339	2473	77	Ir	0.131	0.185	2716
10	Ne	1.030	7.25	25	44	Ru	0.238	0.282	2523	78	Pt	0.133	0.213	2042
11	Na	1.255	2.24	371	45	Rh	0.243	0.306	2233	79	Au	0.129	0.241	1336
12	Mg	0.983	1.35	922	46	Pd	0.243	0.354	1825	80	Hg	0.139	0.378	234
13	Al	0.903	1.05	933	47	Ag	0.235	0.394	1234	81	Tl	0.129	0.314	577
14	Si	0.713	0.670	1685	48	Cd	0.231	0.461	594	82	Pb	0.128	0.313	601
15	P	0.769	1.33	702	49	In	0.233	0.504	430	83	Bi	0.124	0.272	545
16	S	0.708	0.995	388	50	Sn	0.219	0.434	505	84	Po	0.126	0.300	527
17	Cl	0.493	3.14	172	51	Sb	0.208	0.374	904	85	At	0.129	0.289	500
18	Ar	0.520	3.87	84	52	Te	0.202	0.388	723	86	Rn	0.0936	0.755	202
19	K	0.837	1.83	337	53	I	0.214	0.458	387	87	Fr	0.146	0.447	289
20	Ca	0.656	1.04	1112	54	Xe	0.158	1.29	161	88	Ra	0.130	0.299	1233
21	Sc	0.568	0.766	1812	55	Cs	0.241	0.635	302	89	Ac	0.121	0.276	1323
22	Ti	0.524	0.639	1943	56	Ba	0.209	0.488	1002	90	Th	0.118	0.230	2023
23	V	0.489	0.567	2175	57	La	0.199	0.413	1193	91	Pa	0.120	0.225	1703
24	Cr	0.448	0.454	2130	58	Ce	0.192	0.457	1071	92	U	0.116	0.211	1405
25	Mn	0.479	0.582	1517	59	Pr	0.202	0.522	1204	93	Np	0.124	0.213	913
26	Fe	0.452	0.488	1809	60	Nd	0.190	0.492	1289	94	Pu	0.131	0.211	913
27	Co	0.421	0.510	1768	61	Pm	0.190	0.502	1573	95	Am	0.106	0.225	1268
28	Ni	0.445	0.509	1726	62	Sm	0.181	0.453	1345	96	Cm	0.112	0.291	1613
29	Cu	0.384	0.522	1356	63	Eu	0.176	0.468	1090	97	Bk	0.115	0.308	1259
30	Zn	0.389	0.637	693	64	Gd	0.166	0.434	1585	98	Cf	0.117	0.308	1173
31	Ga	0.374	0.590	303	65	Tb	0.182	0.461	1630	99	Es	0.115	0.305	–
32	Ge	0.332	0.428	1210	66	Dy	0.172	0.461	1682	100	Fm	0.114	0.301	–
33	As	0.330	0.489	888	67	Ho	0.164	0.454	1743	101	Md	0.110	0.292	–
34	Se	0.322	0.533	494	68	Er	0.168	0.438	1795	102	No	0.108	0.263	–

strate the natural incorporation of lanthanides and actinides and the respective even chemical elements in the proposed entropy system. This is also evident from Table 2. These elements are commonly assigned to an isolated unicellular group.

In the group of odd elements, a wide entropy variation is typical of varicolored polymorphous modifications of phosphorus. Figure 2 presents characteristics of the red phosphorus best corresponding to its group position in the Bi–Sb–As–P series. In general, chemical elements in the entropic systems unequivocally corre-

spond to groups of the periodic system. Only their extreme positions are shown in Figs. 2 and 3. Deep entropy minimums link the most refractory substances. Tungsten (3693 K) and rhenium (3453 K) are the most refractory elements after graphite and diamond. The low specific entropies of these elements is linked with a low specific heat capacity. An increase in these parameters generally correlates with a decrease in the melting temperature.

In contrast to the minimal entropic positions of the elements, the maximal positions falling on the alkali

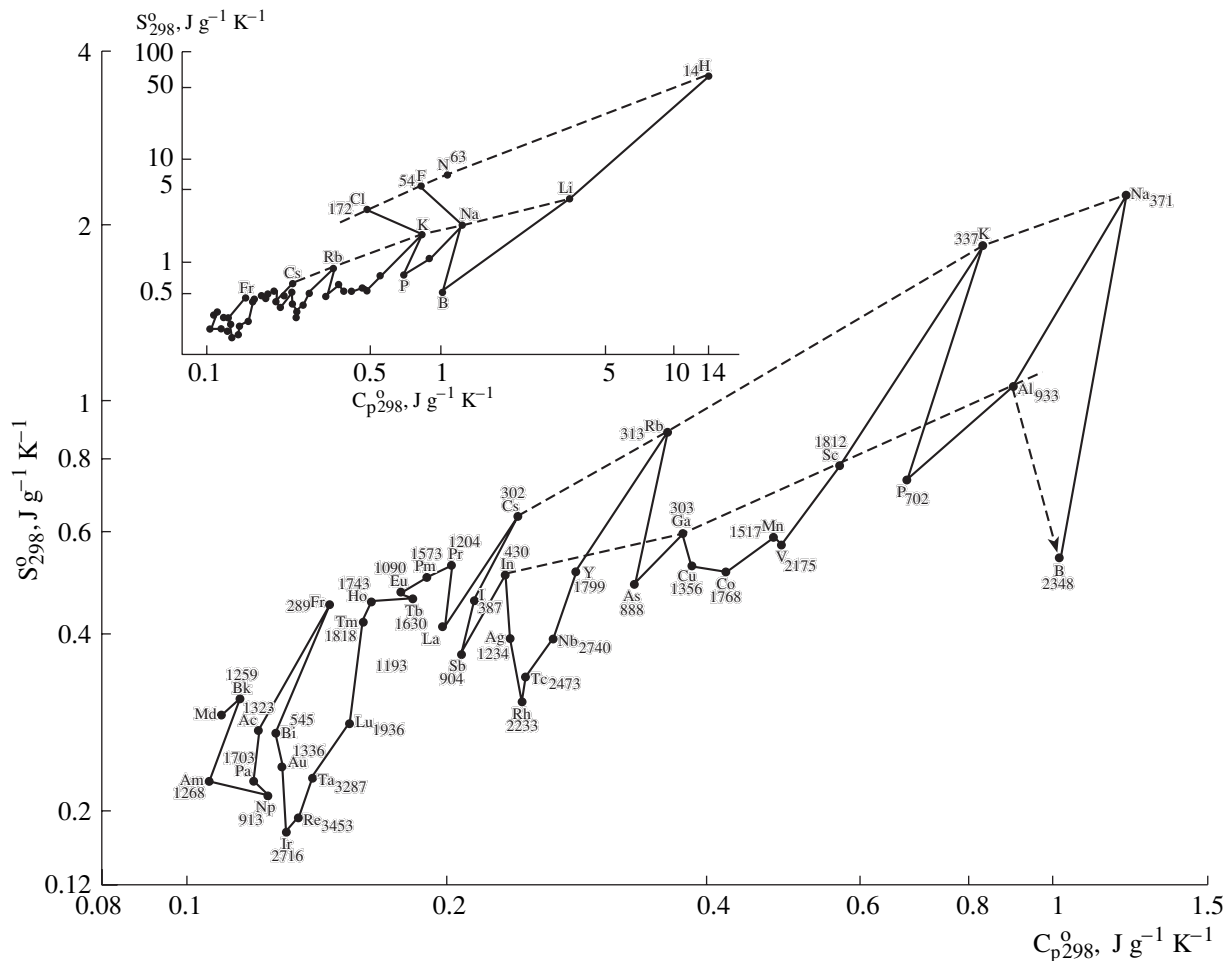


Fig. 2. Periodicity in entropy and heat capacity variation of elementary substances corresponding to the odd chemical elements (melting temperature is also shown). Here and in Fig. 4, the dashed arrows indicate the chemical elements with anomalously low entropy values.

and alkali-earth metals reflect the fusible properties of respective elementary substances. The main series of entropy maximum is Zn, Cd, Hg, In, Ga, and Tl. The melting temperature of these elements is even lower than that of alkali and alkali-earth metals.

The correlation of thermodynamic and physical properties of elementary substances corresponding to the chemical elements demonstrates the fundamental character of the relationships (Figs. 2, 3), which are considered to be a basis of geochemical systematics of elements partly discussed in [1]. Here we focus only on its biogeochemical aspect.

The chemical elements most important for vital activity are C, H, N, O, S, P, and Cl. Ions of Na, K, Ca, and Mg, transitional light metals (V, Mn, Fe, Co, Ni, Cu, Zn), and heavy metals (W, Mo) are also fundamental [6]. The transitional metals take an active part in fermentative reactions of the cellular metabolism. They enter the abovementioned entropic systems (Figs. 2, 3) and correlate with major biophile elements (C, P, and S) in terms of their entropic positions. The outlined natural

series are denoted in Fig. 4 with Roman numerals. The entropic level of metals rises according to the sequence of these numerals. Thus, they resemble biophile elements (Cl, O, and N) that occur as gases under standard conditions.

The entropic characteristics of elements in many respects reflect their role in biological systems. Tungsten, as the lowest entropic element in the series of transitional “biometals,” provides the basis of fermentative metal-catalysis [7]. Tungsten is involved in fermentative reactions by microorganisms (dehydrogenases and oxygenases) together with S-bearing iron albumen in the extremely thermophilic and ordinarily thermophilic microorganisms. Tungsten probably functioned in the active center of metal ferments of the incipient hydrothermal biosystems. All of the currently known tungsten ferments catalyze the redox reactions with an extremely low potential. Primitive hydrogenase, i.e., formation of a transmembrane electrochemical potential, is related to tungsten.

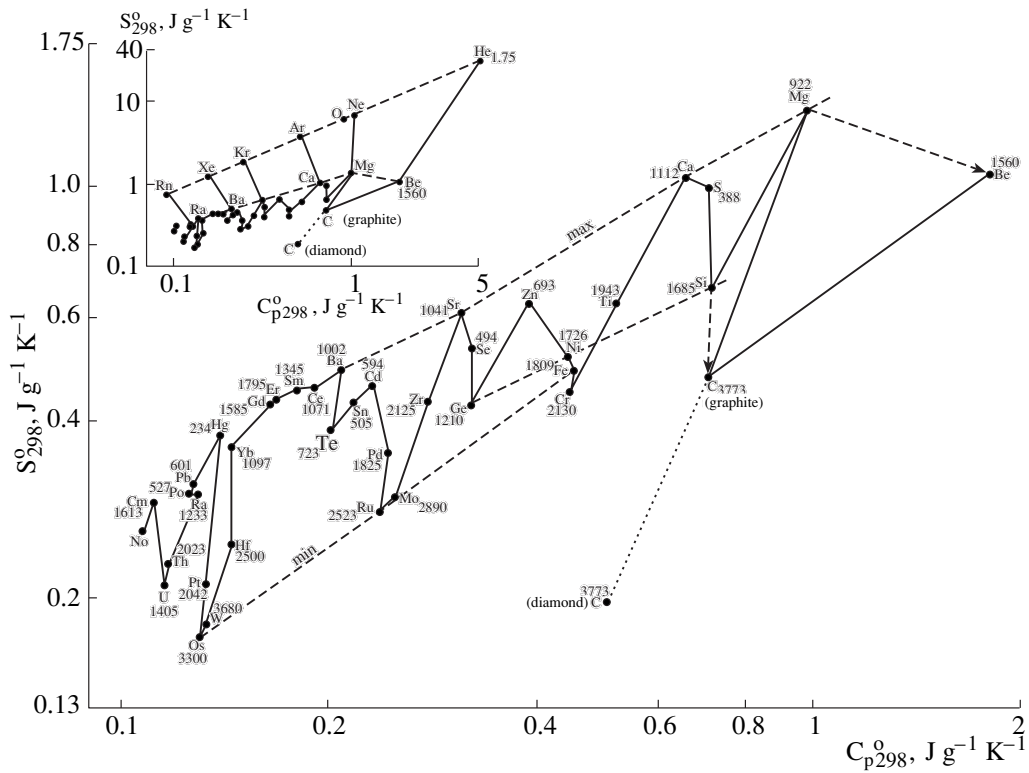


Fig. 3. Periodicity in entropy and heat capacity variation of elementary substances corresponding to the even chemical elements (melting temperature is also shown).

Molybdenum is another transitional heavy metal participating in catalytically active ferment centers. It catalyzes the majority of reactions pertaining to nitro-

gen metabolism. The biochemical similarity of odd elements W, Mo, and Fe is clearly coordinated to their low entropic levels (Figs. 3, 4).

Table 2. Periodic system of elements based on thermodynamic principles

Odd chemical elements

			85At					53I		35Br		17Cl	9F	1H	0	Groups
101Md	95Am	91Pa	87Fr	79Au	89Tm	63Eu	59Pr	55Cs	47Ag	37Rb	29Cu	19K	11Na	3Li	I	
103Lr	97Bk	93Np	89Ac	81Te	71Lu	65Tb	61Pm	57La	49In	39Y	31Ga	21Sc	13Al	5B	III	
105Db	99Es			83Bi	73Ta	67Ho			51Sb	41Nb	33As	23V	15P	7N	V	
107Bh					75Re					43Tc		25Mn			VII	
109Mt					77Ir					45Ph		27Co				

→ Cp°298

Even chemical elements

			86Rn					54Xe		36Kr		18Ar	10Ne	2He	0	Groups
102No	96Cm	92U	88Ra	80Hg	70Yb	84Gd	60Nd	56Ba	48Cd	38Sr	30Zn	20Ca	12Mg	4Be	II	
104Rf	98Cf	94Pu	90Th	82Pb	72Hf	66Dy	62Sm	58Ce	50Sn	40Zr	32Ge	22Ti	14Si	6C	IV	
106Sg	100Fm			84Po	74W	68Er			52Te	42Mo	34Se	24Cr	16S	8O	VI	
108Hs					76Os					44Ru		26Fe			VIII	
110					78Pt					46Pd		28Ni				

→ Cp°298

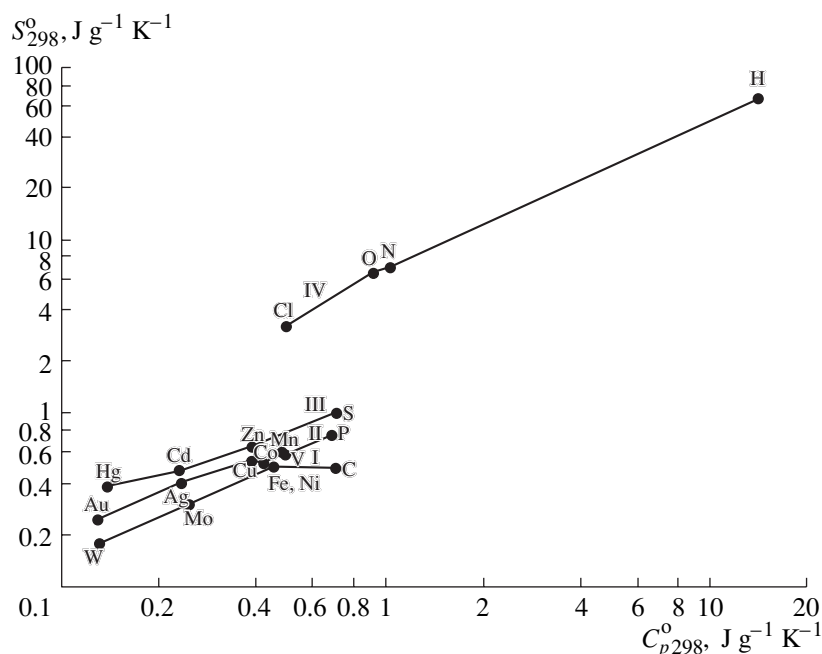


Fig. 4. Biogeochemical elements divided into series (denoted by Roman numeral in order of increasing entropy level).

The transitional light metals control the main energetic functions of microorganisms, e.g., breathing (Fe, Cu), fixation of molecular nitrogen (Fe, V, Mo), and photooxidation of water (Fe, Mn). The most important role belongs to the cytochromes (Fe, Cu, Co, Ni) as electron carriers. Catalases, peroxidases, and superoxidases–dismutases (Fe, Cu, V, Mn) also serve as redox-convertors of active oxygen forms. Comparison of porphyrin and corrin metal complexes as the critical cofactors in many fermentative reactions is important. The nickel–tetrapyrrol coenzymes (Ni) as cofactors of the methyl–cobalt reductase are hybrids between corrin (Co) and porphyrin (Fe). The thermodynamic diagram (Fig. 4) demonstrates that they elucidate an evolutionary relationship between Co-bearing corrin and Fe-bearing porphyrin systems [9, 10].

Thus, transitional metals are incorporated into ferments, vitamins, and hormones. In addition, they are used as final electron acceptors during processes of mineralization in the biosphere [11]. The fermentative dissimilatory reduction and mineralization of some of these elements, e.g., Fe(III), Mn(IV), Co(III), Cr(IV), Pd(II), and Au(III) give rise to the formation of ore deposits.

The role of heavy metals from the zinc (Cd, Hg) and copper (Ag, Au) groups remains ambiguous in many respects. The microbiological transformation, with participation of membrane redox-carriers and oxidoreductases, was established for gold [12, 13].

The chemical elements shown in Fig. 4 are vital for cell activity. They naturally fit into vital processes and are “biometals” often involved in microbial ore formation. However, many other metals remain ignored in

this respect [14]. Elements used by bacteria in sedimentary ore deposition and other specific metals that are biologically induced and concentrated as secondary products of interaction between the microorganism and the environment fit into this category.

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