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GEOCHEMISTRY

Metallogenic and Biogeochemical Systematics of Transition Metals

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A thermodynamic approach to the systematics of chemical elements on the basis of the specific quantities (J g^{-1} K^{-1})—heat capacity ($C^0_{p\,298}$) and entropy (S^0_{298})—of the respective elementary substances has been developed in [1, 2]. The metals transitional from *s*-elements (Ca, Sr, Yb, and No) to *p*-elements (Ga, In, and Te) are considered in this communication in thermodynamic terms. In the periodic system, they are represented by four periods (ordinal numbers of metals are shown in parentheses): period 4 (21–30), period 5 (39–48), period 6 (71–80), and period 7 (103–112). Metals of period 7 are not considered in this communication. The specific heat capacity, entropy, and melting temperature of the transition metals are given in Table 1.

As do most chemical elements, the transition metals obey the Oddo–Harkins rule and are subdivided into metals of odd and even ordinal numerals in terms of their abundance (Fig. 1). This subdivision displays the specific thermodynamic features of the transition metals and is traced by correlations of their heat capacity and entropy (Fig. 2) demonstrating that the odd and even metals make up autonomous periodic subsystems (Table 2). The transition metal oxidation states expressed in their chemical compounds is also shown in Table 2. Except for the metals of groups III and IV, which have constant valences, the transition metals readily change their oxidation state. This is responsible to a great extent for their metallogenic specialization and biochemical function. The variations of heat capacity and entropy of transition metals are principally different. As can be seen from Fig. 2, the specific heat capacity of the metals varies monotonously, whereas entropy passes in each period through deep minimums, falling at Co–Rh–Ir in odd metal series and at Fe (Cr)–Ru–Os in even metal series. On the contrary, entropy maximums separate the periods of transition metals (Fig. 2). The entropy of metals inversely correlates with the stability of their solid (crystalline) state, so that the entropy maximums coincide with minimal melting temperatures of metals (Zn–Cd–Hg, Cu–Ag–Au), while the low-entropy metals have the highest melting

Table 1. Specific heat capacity and entropy (J · g^{-1} · K^{-1}) and melting temperature (K) of elementary transition metals

Period	Metal		$C^\circ_{p\,298}$	S°_{298}	T
4	21	Sc	0.568	0.766	1812
	22	Ti	0.524	0.639	1943
	23	V	0.489	0.567	2175
	24	Cr	0.448	0.454	2130
	25	Mn	0.479	0.582	1517
	26	Fe	0.452	0.488	1809
	27	Co	0.421	0.510	1768
	28	Ni	0.445	0.509	1726
	29	Cu	0.384	0.522	1356
	30	Zn	0.389	0.637	693
5	39	Y	0.282	0.517	1799
	40	Zr	0.278	0.428	2125
	41	Nb	0.265	0.394	2740
	42	Mo	0.249	0.299	2890
	43	Tc	0.246	0.339	2473
	44	Ru	0.238	0.282	2523
	45	Rh	0.243	0.306	2233
	46	Pd	0.243	0.354	1825
	47	Ag	0.235	0.394	1234
	48	Cd	0.231	0.461	594
6	71	Lu	0.154	0.282	1936
	72	Hf	0.144	0.244	2500
	73	Ta	0.140	0.229	3287
	74	W	0.132	0.178	3680
	85	Re	0.135	0.196	3453
	76	Os	0.123	0.171	3300
	77	Ir	0.131	0.185	2716
	78	Pt	0.133	0.213	2042
	79	Au	0.129	0.241	1336
	80	Hg	0.139	0.378	234

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Table 2. Periodic subsystems of odd and even transition metals with reference to their oxidation state in chemical compounds (subordinate oxidation states are shown in parentheses)

S^0_{298}	^{79}Au 1.3	^{47}Ag 1.2	^{29}Cu 1.2		I	Groups
↑	^{103}Lr 3	^{71}Lu 3	^{39}Y 3	^{21}Sc 3	III	
	^{105}Db 5	^{73}Ta 5, (3)	^{41}Nb 5.3	^{23}V 5, (2, 3, 7)	V	
	^{107}Bh	^{75}Re 7, (2, 4)	^{43}Tc 4.7	^{25}Mn 2, 3, 4, 5, (7)	VII	
min	^{109}Mt	^{77}Ir 1, 4, (2, 3,6)	^{45}Rh 1, 3, (2, 4)	^{27}Co 2, 3		
	$\longrightarrow C^0_{p298}$					
S^0_{298}	^{80}Hg 2, (1)	^{48}Cd 2	^{30}Zn 2		II	Groups
↑	^{104}Rf 4	^{72}Hf 4	^{40}Zr 4	^{22}Ti 4, (3)	IV	
	^{106}Sg	^{74}W 4, 5, 6, (2, 3)	^{42}Mo 2, 4, 5, 6, (3)	^{24}Cr 3, 6, (2)	VI	
min	^{108}Hs	^{76}Os 2, 4, 6, 8, (3)	^{44}Ru 3, 4, (8)	^{26}Fe 2, 3, (6)	VIII	
↓	^{110}Uun	^{78}Pt 2, 4	^{46}Pd 2, 4	^{28}Ni 2.3		

temperatures (Fig. 3). However, the entropy minimums (Table 2) and maximal melting temperatures do not show complete consistence. The entropy minimums fall at Co–Rh–Ir and Fe (Cr)–Ru–Os, whereas the maximal melting temperatures fall at V–Nb–Ta and Cr–Mo–W.

The entropy minimums (Cr and refractory PGE) divide the transition metals of each period into families that are distinguished by the character of correlation between heat capacity and entropy (Fig. 2). The negative relationship of these parameters (left branches of the extremums) is typical of sulfurophile (chalcophile) and siderophile metals with a strong trend toward occurring in the native state, e.g., Fe–Ni–Co–Cu–Zn (period 4), Ru–Rh–Pd–Ag–Cd (period 5), and Os–Ir–Pt–Au–Hg (period 6). In contrast, the positive correlation between heat capacity and entropy (right branches) is typical of oxyphile metals, e.g., Mn–V–Ti–Sc (period 4), Mo–Tc–Nb–Zr–Y (period 5), and W–Re–Ta–Hf–Lu (period 6). This radical partition of transition elements is manifested in their autonomy in different zones of ore deposits and relationship with different types of magmatism. Deposits of siderophile and sulfurophile metals are genetically related to primitive mafic and ultramafic mantle magmatism. In contrast, the oxyphile metals are confined to the crustal igneous rocks and the higher level of mantle magmatism evolution with an alkaline trend.

Ore deposits form as a result of the segregation of magmatic differentiates, which can selectively extract the transition metals from the transmagmatic fluids that accompany the magmatic activity. These differentiates are commonly enriched in iron, chromium, and salt components. They make up ore units (reefs) in the stratiform intrusions or participate in the hydrothermal activity to form ore deposits beyond the intrusive bodies. The hydrothermal activity may reach platformal or oceanic depressions and be involved in biochemical and other types of sedimentary ore deposition, because the microorganisms possess a unique ability to concentrate dispersed metals [4], including the transition metals (V–Mo–W–Mn–Fe–Co–Ni–Cu–Zn), which, according to the biochemical periodic system, are the major biological transition metals [5]. The high heat capacity of these transition metals is among the main thermodynamic parameters that control their functioning in the enzymatic redox systems of microorganisms, because all of the biological metals listed above, except Mo and W, belong to period 4 of the periodic system. Chromium located between Mn and V in the periodic system should also be included in the family of biological transition metals. However, the anomalously ordered rigid structure of Cr, which is responsible for its lower entropy relative to that of group 4 metals (Fig. 2), hampers the introduction of Cr into the macromolecular structures of microorganisms. Therefore, they formed enzymatic structures with other metals of Cr group, namely Mo and W, despite their relatively low heat capacity (Table 1). Thus, the impossibility of forming Cr-containing enzymes was compensated for by the formation of Mo- and W-containing enzymes.

The unique character of the coordination chemistry of Mo and W in active enzyme centers is related to their ability to couple a soft process transferring two electrons of an oxygen atom between water and a substrate. These metals also serve as successive single-electron carriers owing to the redox reactions M(VI)/M(IV), M(V)/M(IV), and M(VI)/M(V), where M is Mo or W [6]. The Mo-containing enzymes catalyze the main metabolic reactions of the sulfur, carbon, and nitrogen cycles. Tungsten is probably coenzyme of the first redox metalloenzymes in the evolution cycles [7]. The existing four W-containing enzymes catalyze the metabolic reactions with an extremely low redox potential ranging from –580 mV. In these reactions, tungsten is bound to one or two pterin molecules (as in molybdoenzymes) and can replace Mo in the molybdenum cofactors (FeWco), while dimethylsulfoxyreductase may contain Ni, Mo, or W in the active center and make up a family of reductases [8]. This family also includes the mem-

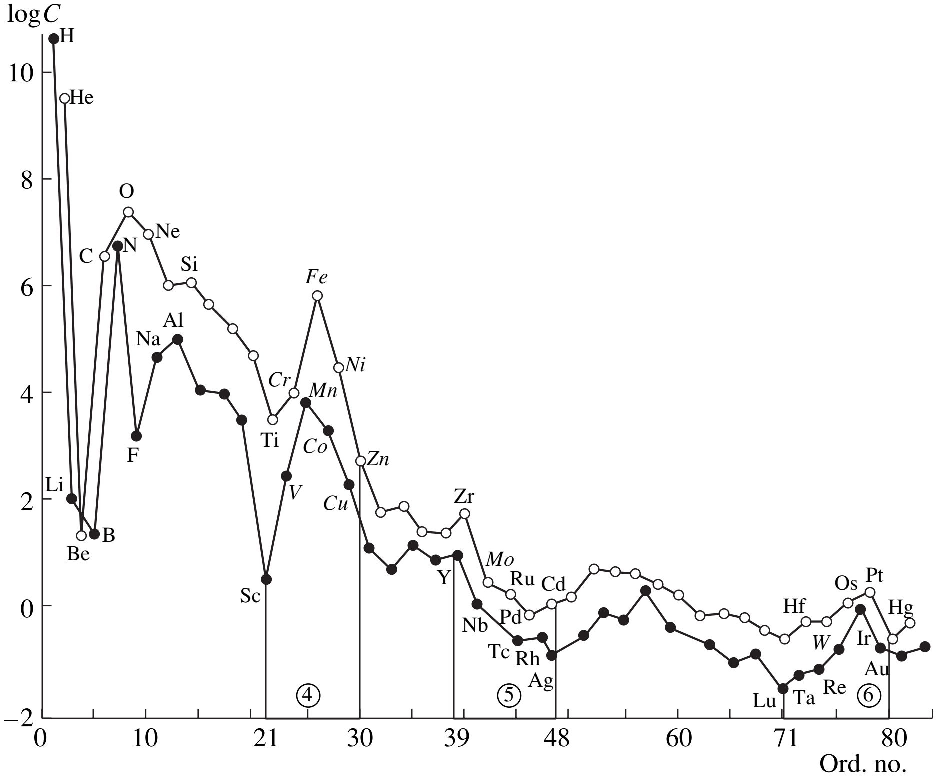

Fig. 1. Location of transition metals (periods are designated by numerals in circles) on the diagram of odd (filled circles) and even (open circles) chemical elements (after [3, p. 100]). The major biological transition metals are italicized.

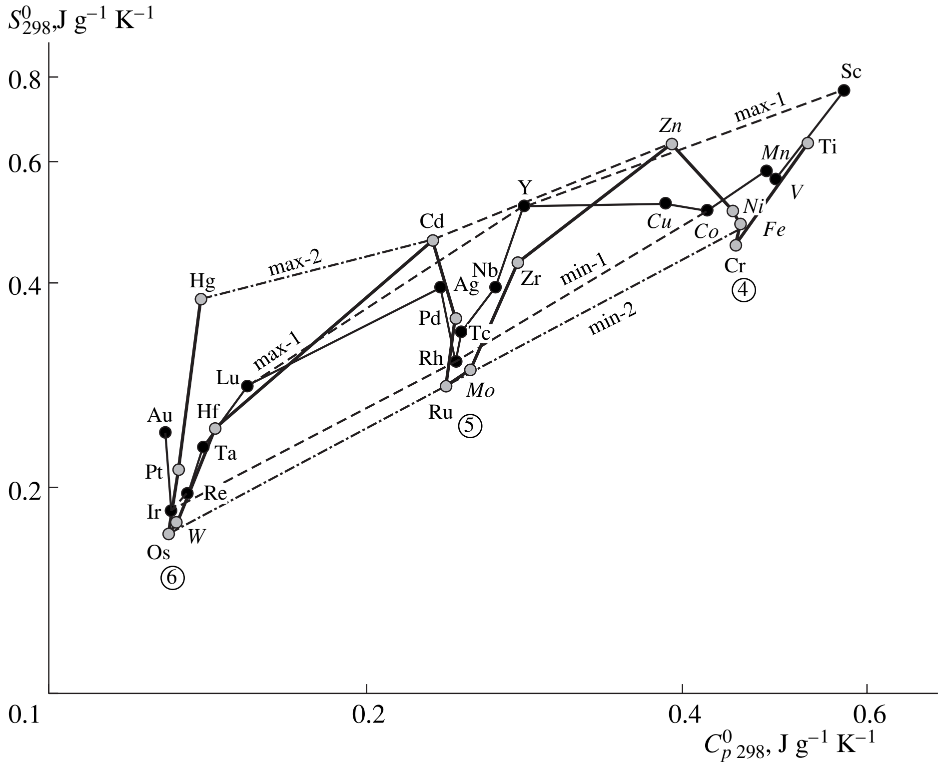

Fig. 2. Entropy of transition metals vs. their heat capacity. See Fig. 1 for legend. Groups of metals with extreme entropy values are shown by dashed lines.

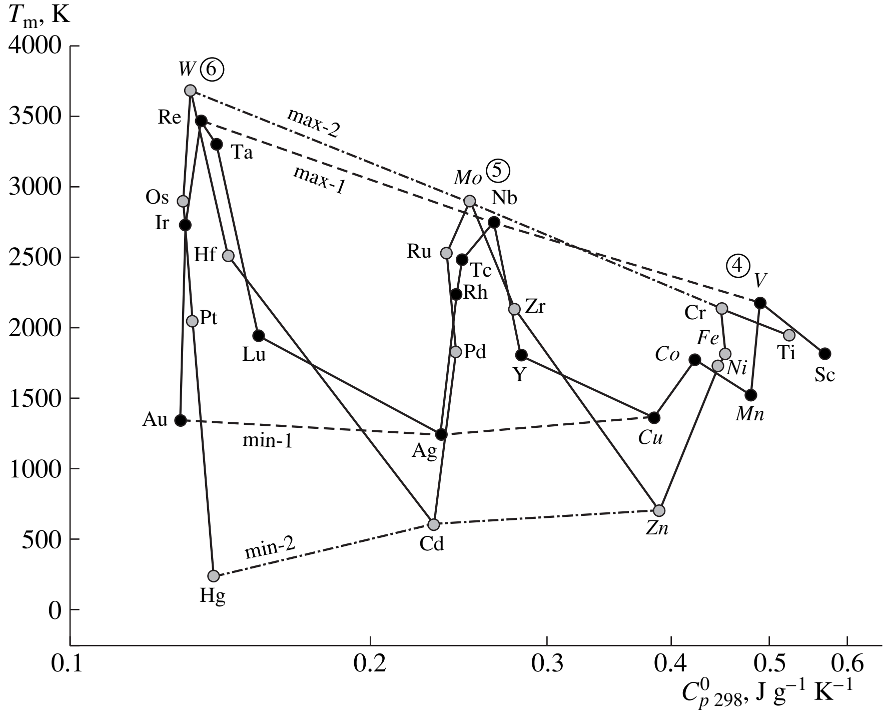

Fig. 3. Variation periodicity of melting temperature (T_m) of transition metals vs. their heat capacity. See Fig. 1 for legend. Maximal and minimal melting temperatures of (1) odd and (2) even metals are shown by dashed lines.

brane-bound Ni,Fe-hydrogenase (formation of electrochemical transmembrane potential) and sulfur reductase of thermophile and acidophile microorganisms [9]. In addition, Fe, Ni, Mo, and W are necessary for CO_2 reduction by molecular hydrogen in the process of methanogenesis [10]. Thus, we can outline the bioparageneses of the even transition metals characterized by low entropy in their periods, i.e., W–Mo–Fe (Ni) (Fig. 2).

Microorganisms are active agents of biogenic ore formation that involves the transition metals in metabolic processes [4]. This is true for not only the main biometals considered above, but also for a number of other metals involved in binding, transport, oxidation, reduction, and methylation. These transition metals are distinguished by low heat capacity. Except for Sc and Ti, they belong to periods 5 (Y, Tc, Ru, Rh, Pd, Ag, and Cd) and 6 (Lu, Pt, Au, and Hg). The biotransformation of Zr, Nb, Hf, Ta, Re, Os, and Ir has not to date been ascertained [5].

Microorganisms that retain their vital activity up to 120°C [11] play a special role in sedimentary ore formation. Hydrothermal fluids ascending from deep magmatic sources undergo acid–alkaline differentiation in the course of cooling [12] and commonly reach the surficial water reservoirs in a bimodal state with average pH values corresponding to the acid (1–3), neutral, or subalkaline (7–9) region [13]. Thermophile microorganisms are subdivided into the acido-, neutro-, and alkalophile groups, respectively. In ore-containing systems, they promote the development of bonds between endo- and exogenic processes, for example, in the mid-oceanic ridges, where the formation of massive sulfide ore is accompanied by the system of black smokers on the oceanic floor.

The study of the early microbiological mineral respiration made it possible to understand the mechanism of transformation of some transition metals into minerals by hyperthermophile *Bacteria* and *Archaea* pertaining to the 16S rRNA branch of the life tree [14]. At present, the dissimilatory enzymatic reduction of transition metals is established in the following periods: Cr(VI)/CR(III), Fe(III)/Fe(II), Co(III)/Co(II), Mn(VI)/Mn(IV), and Mn(IV)/Mn(II) in period 4; Tc(VII)/Tc(IV) and Pd(II)/Pd(0) in period 5; and Au(III)/Au(0) in period 6. Metals of periods 5 and 6 (Pd and Au) have a low heat capacity and serve as end acceptors in the electron transport chain of thermophile *Bacteria* and *Archaea.* Therefore, they are enzymatically reduced to the native state without energy storage by microbial cells. In contrast, the dissimilatory reduction of period 4 metals (Cr, Fe, Co, and Mn) with a high heat capacity (Fig. 2, Table 2) coupled with oxidation results in energy storage by cells [15] (for example, a transmembrane electrochemical potential is generated in the course of H_2 oxidation). All II, III, and IV group metals characterized by stable oxidation degree (Table 2) are not reduced in dissimilatory enzymatic processes. Thus, a difference in the thermodynamic properties of transition metals may promote various biochemical mechanisms that determine the behavior of transition metals in exogenic ore formations.

The transition metals are largely siderophile elements. They became concentrated mainly in the liquid Ni–Fe core during the primary layering of the Earth, so that its primary silicate shell was sterile with respect to the transition metals. Magmatism originated and developed in this shell under the influence of core-derived metalliferous fluids controlling the geochemical specialization (with respect to the transition metals) of both primary magmas and all derivatives of the interaction with transmagmatic fluids. Therefore, the intrusions are commonly surrounded by aureoles of transition metals in country rocks. The metallogenic specialization of magmatism arises only under specific conditions of transition metal concentration by fluid-magmatic systems and the consequent processes of endo- and exogenic ore formation. Biological transformation and concentration of transition elements take place during the exogenic ore formation.

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