

Geochemical Model of Early Earth's Surface Systems, based on Extended Conception of Ionic Potential

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In geochemical modeling of formation and evolution of the early Earth's surface systems, Goldschmidt's conception of geochemical division of elements according ionic potential (Goldschmidt, 1937) is useful but only particularly, as is restricted to cations. The recently established geochemical division both cations and anions - *extending conception of ionic potential* (ECIP), (Dangi), 1997; 1998) open new approaches to the problem.

In the new geochemical model of composition/evolution of early Earth's surface systems, 5 geochemical stages are defined: (1) Pre-hydrosphere s.: high temperature anoxic systems: *atmosphere*- H₂, He, H₂O(g); lithosphere- basaltic; (2) Hydrosphere formation s.: lower temperature anoxic systems; *pre-oceanic hydrosphere*, consisting of isolated basins, contains as dissolved compounds, according ECIP: anions of redozates (AR), soluble anions (SA), soluble cations (SC) (Table 1); (3) Proto oceans s. - water cycle started, anoxic systems: *atmosphere*- more CO₂, N₂, H₂O; *isolated oceans*- vary in composition: Mg²⁺, Ca²⁺, Fe²⁺, Cl⁻, CO₃²⁻, S²⁻; Sediments rich in Fe²⁺, with sulfides; weathering crusts poor in Fe.

Table 1. Geochemical assemblages in oceanic water in stages 3-4 (anoxic) and 5 (oxic).

Groups of elements according ECIP	Stages 3-4 (anoxic)	Stage 5 (oxic)
Anions of redozates	S ²⁻ , Se ²⁻	
Soluble anions	Cl ⁻ , F ⁻ , J ⁻ , Br ⁻	Cl ⁻ , F ⁻ , J ⁻ , Br ⁻
Soluble cations	Na ⁺ , K ⁺ , Ca ²⁺ Mg ²⁺ , Fe ²⁺ , ...	Na ⁺ , K ⁺ , Ca ²⁺ Mg ²⁺ , ...
Elements of hydrolyzates		U ⁶⁺
Complex soluble anions		SO ₄ ²⁻ , SeO ₄ ²⁻

(4) Anoxic ocean s.: world ocean; anaerobic organisms; anoxic systems: *atmosphere*- rich in CO₂, N₂; H₂S stable; *Ocean*- acid, with AR (S⁻, Se⁻), SA (Cl⁻, J⁻), SC (Na⁺, Ca²⁺, Mg²⁺, Fe²⁺), CSA (CO₃⁻, PO₄³⁻); *weathering*: kaolin/bauxites depleted in Fe; *sediments* Fe-rich; (5) Early oxic ocean s. - O₂ in atmosphere, aerobic organisms, oxic systems: *world ocean*-sulphate, selenate present; *weathering*- kaolin/bauxites Fe-rich (Fe³⁺), increased Th/U ratio; *sediments* with sulphates (Fig. 1, field 2); ocean/atmosphere- oxic capacity low, oscillated: deposition of Fe-banded formations (Fe²⁺+Fe³⁺ bands) (started ≥3.5 b.y. ago).

References

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Geochemical Model of Lead in Supergenic Systems: Mobility, Impacts of Cerusite and Fe-oxyhydroxides

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In supergenic systems (SS)- sediments, soils, weathering crusts, surface- and groundwaters, lead may be more or less common. As a soluble cation (according ionic potential), Pb may enter into surface/groundwaters, but its mobility may be strongly restricted by some geochemical processes. We have studied two most important of them: formation of cerusite and co-precipitation with Fe-oxyhydroxides, in field and in experimental systems (Tables 1-3). In field studies covered the cerusite deposit/mine Olovo, the iron-arsenic-sulphate mineral water Crni Guber (in Bosnia) and the Danube River (in Serbia) (Dangic & Dangic, 1989; 2001). Olovo deposit (ore=cerusite+galena+calcite) is situated in limestones and crossed by a river (river 1, inflow into river 2). The Crni Guber at the spring forms Fe-oxihydroxides (with jarosite). Danube is the second biggest European River.

Based on all studies, a thermodynamic model of lead mobility is established. The field stabilities at related pH-Eh diagram, indicated that formation/solubility of cerusite regulate Pb-content in near-neutral to higher pH-domains (rivers, springs), and of Fe-oxyhydroxide in low-lower pH and low-Eh domains.

Table 1. Waters in the environment of cerusite mine Olovo: lead content (in ppb), pH and Eh.

	Pb _t	Pb _d	Pb _d /Pb _t	pH	Eh (V)
Mine-580m	8.6	2.4	0.28	8.00	0.391
Mine-680m	280	47.5	0.17	7.62	0.394
Springs	2.5	2.0	0.80	7.25	0.419
River 1	4.5	4.5	1.00	8.20	0.394
River 2	4.2	1.5	0.36	8.30	0.396

Pb_t= total lead; Pb_d= dissolved lead.

Table 2. Lead content in the Crni Guber Sring system.

	Water (W)	Sediment (S)	S/ W	Jarosite
Pb	46 ppb	1000 ppm	22000	1-12 %
Water: pH=3.6; Eh=0.470 V; Fe ²⁺ =125 ppm; SO ₄ ²⁻ =526 ppm				

Table 3. Lead in water (ppb): ore-water experimental systems.

Solid components (S)	Water: S	pH---Pb	pH---Pb
Cerusite+Limestone	9:1	7.5—70	8.0—40
Cerusite+Galena+Limst.	9:1	7.5—25	8.0—4

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