GEOELECTROCHEMICAL PHENOMENA IN PLACER DEPOSITS. PROBABLE ROLE OF ELECTROCHEMICAL FIELDS AS A WHOLE FOR GENERATION OF REGOLITH.

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ABSTRACT

As a rule, interpretation of regolith formation is done at present without reference to electrical energy. Exceptions are studies that describe processes of oxidation and reduction in sulphide deposits. The three examples considered in this article propose significant participation of electrical energy, and therefore electrochemical processes in the transformation of geological environments.

Key words: geoelectrochemistry, electrofiltration potential, liquid-junction self-potential, dissolution, migration, accumulation, ion

INTRODUCTION

Significant transformation of rocks takes place in the huge areas with regolith development between 30°N - 30°S (Smith, 1996). The rocks are reprocessed and altered as a whole to the depths of up to 500 meters and, in areas with ancient crust, weathering alteration can be seen to depths of 2-3km (rich oxidized ores of Krivorozhsky type).

The largest supergene deposits of Al, Fe, Mn, Ni, Co, Ti, Au and other metals are known in the areas of regolith development. Their generation is often accompanied by segregation into monomineralic forms. This phenomenon is associated with matter separation. The processes involved can probably proceed only with energy input because any such concentration process cannot be spontaneous (Safronov, et al, 1978).

Sources of energy under surface and near-surface conditions include:

- active water exchange with mechanical transfer of surface and underground waters in response to pressure gradients (filtration of solutions);
- solar energy which induces active biologic processes; the importance of this type of energy, manifested through living matter, was first noticed by V.I.Vernadsky as early as the 1920s (1955);
- chemical potential gradients (especially interact with near-surface oxidizing environments abyssal rocks and the boundary between fresh and saline waters).

The gradients of pressure, temperature, and concentration gradients inevitably create electrical potential gradients within geological environments. A wide spectrum of electrical energy form has been revealed within earth and they manifest as filtration, diffusion-absorption, galvanic and others local electrical fields(Kunory et al, 1955, Keller and Frischknecht, 1966, Semenov, 1968,Sheriff, 1974).These natural electrical fields may exist for a long time depending on the duration of the geological processes, which are creating their. The energy of such fields may be of the order of 10-100 joules/cm^2.

The main electrochemical processes operating in the geological environment are associated with dissolution and deposition of matter, migration of dissolved components within an electric current field, as well as the accumulation of matter within specific parts of the field. It is not possible to cover the whole range of problems associated with the role of electrical energy in the formation of regolith in this paper. These geological "problems" have been chosen for discussion to illustrate electrochemical concepts.

The three examples to be discussed are:

- Mineral genesis in deposits of placer gold and other native elements (Voronin and Goldberg, 1972)
- "Uphill" movement or migration of metals and their accumulation compared with concentration gradient (Alekseev and Dukhanin, 1989; Alekseev, Goldberg and Dukhanin,1989a, 1989b)
- Formation of rich oxidized iron ores of the Krivorozhsky type (Goldberg et al, 1988).

MINERAL GENESIS IN PLACER DEPOSITS OF GOLD AND OTHER NATIVE ELEMENTS.

There are number of features of placer deposits that, in the written opinion, have not been satisfactory explained For particular, whereas placer form in oxidizing environment some the processes appear to be reducing in character Some characteristics of placer deposits are as follows:

1. Native metals found in the earth's crust occur more often in placers than in bedrock;
2. All placer metals (Zn^0, Fe^0, SnO, Pb^0, Bi^0, Cu^0, As^0) except for gold, platinum group metals and mercury, - are unstable under normal surface conditions;
3. Native metals in placer occur in mutual intergrowths, that are unknown in bedrock sources These include Pt-Pb, Sn-Pt, Sn-Au and some other unusual metal associations (Vernadsky, 1955)

Vernadsky (1955) suggested of native metals directly in placers This was confirmed by finding secondary gold, overgrown over primary gold The secondary gold is usually developed on one side of a primary gold grain (Fig 1) Such asymmetric gold growth, which can be distinctly seen in microsections and has been described in a number of papers (Iabloneva, 1965), has nevertheless, never been explained

Figure 1: *Dendritic branches of "new gold" from placer deposit (after Iabloneva, 1965) 7x*

The observations outlined above demonstrate a conflict between the oxidizing nature of the environment and apparent reducing process observed in placers

Let us consider this phenomenon from the electrochemical point of view Firstly let us discuss some processes proceeding in alluvial deposits in river valleys where placers are being formed Movement of solutions through porous media results in an electric potential difference This potential difference is known as the streaming potential (E_f) (Semenov, 1968; Bogoslovsky and Ogilvy, 1972 Schiavone, D and Quarto, R , 1984) In Western geophysical literature it is also known as the streaming potential or electrofiltration potential (Sheriff, 1974)

The filtration stream in the natural environment is localized within some volume (riverbed, fractures in rocks, mechanically weak zones) The electrofiltration potential value of a river stream ranges from tens to thousands of mV; especially so in areas of mountain rivers - up to 1 V/km

One of the manifestations of this electrochemical process is in charging electronic conductors A potential difference is generated between the ends of such a conductor, which is defined by the potential decrease in the field corresponding to the length of the conductor Electrochemical reactions caused by cathode reduction and anode oxidation can start at definite potential values on the ends of the conductor The most typical reduction reactions are reactions that precipitate elements out of solutions like (Glasstone, 1956):

$$Me^+ + e^- = Me^0$$

Examples of electronic conductors in placers are particles of gold, platinum, magnetite, graphite etc Experimental investigations using models have been carried out to define possible mechanisms for initiation of electrochemical processes on such particles by the electrofiltration field (Voronin and Goldberg, 1972)

EXPERIMENTAL INVESTIGATION

An electrofiltration field was produced by forcing distilled water through a column of quartz sand (0 1-0 2mm fraction) 2cm long and 1cm2 in cross-section (Fig 2) Potentials were measured relative to standard calomel electrodes using a high-ohm voltmeter Current was measured using a highly sensitive micro-ammeter Platinum wire was used as an electron-conducting electrodes When pressure from 5 to 120mm was measured (corresponding to an elevation difference from 0 06 to 1 6m) the streaming potential varied linearly from 0 1 to 1 3 V

Electric current occurred within the column when platinum electrodes were connected up via a micro-ammeter The current value also varied linearly with pressure variation; current varied from 1×10^{-8} to 4×10^{-7} A

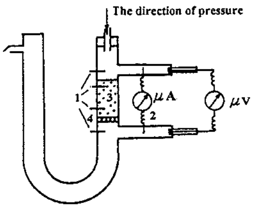

Figure 2: *Electrochemical Nucleus 1 Non-polarizable measuring electrodes 2 Platium electrodes 3 Quartz sand 4 Quartz membranes*

DISCUSSION OF THE RESULTS.

The occurrence of an electric current in the conductor indicates the induction of electrochemical reactions within it. They are observable even at a low electric field potential. The possibility of one reaction or another is defined by the electrode potential and solution composition. In this experiment, the electrode potential, measured on platinum prior to occurrence of the electric field was equal to +0.12V (or +0.3V according to a hydrogene scale). At a current strength of 2×10^{-8} A the potential on the platinum cathode end changed to an anodic value of +0.116 V (or +0.336 V according to the hydrogen scale - h.s.). At current strength of 1×10^{-7} A it was -0.2 V (or -0.05V according to h.s.). The defined potentials are sufficient for precipitation of elements with reduction potentials more positive than the measured values. They include the whole group of elements from Sn^0 to Au^0 listed in Table 1.

Table 1: *Normal electrode potentials*

ELECTRODE REACTION	**(0, V**	**ELECTRODE REACTION**	**(0, V**
$Zn^{2+} + 2e = Zn^0$	-0.763	$Bi^{3+} + 3e = Bi^0$	+0.23
$Cd^{2+} + 2e = Cd^0$	-0.402	$As^{3+} + 3e = As^0$	+0.30
$Co^{2+} + 2e = Co^0$	-0.270	$Cu^{2+} + 2e = Cu^0$	+0.34
$Ni^{2+} + 2e = Ni^0$	-0.230	$Ag^{+} + e = Ag^0$	+0.70
$Pb^{2+} + 2e = Pb^0$	-0.127	$Pd^{2+} + 2e = Pd^0$	+0.83
$Fe^{3+} + 3e = Fe^0$	-0.036	$Hg^{2+} + 2e = Hg^0$	+0.90
$H^{+} + e = H_2^0 1/2$	0.000	$Pt2^{+} + 2e = Pt^0$	+1.20
$Sn^{4+} + 4e = Sn^0$	+0.050	$Au^{3+} + 3e = Au^0$	+1.43
$Sb^{3+} + 3e = Sb^0$	+0.200	$Au^{+} + e = Au^0$	+1.70

Normal electrode potentials are shown for standard conditions. However, under natural conditions, the concentration of metal ions in solution will differ from that under standard conditions and the potential values in the table will be different (Cammann, 1979). The dependence of the electrode potential on ionic activity (activity approaches concentration in dilute solutions) is defined by Nernst equation (Davies and James, 1976). This equation can be used to calculate for example, the gold potential at ionic concentrations corresponding to the average gold content in natural waters 0.002 ppb (Levinson, 1974). The calculated potential (+1.06 V) is much more positive than experimental values. The gold content in waters in auriferous provinces is typically one or two orders of magnitude higher than unmineralised regions (Giblin, A., 1997), and in such cases precipitation from solutions is more likely.

The application of the electrochemical mechanism outlined above in placer deposits may be applied as follows. Abundance of native metals is defined by the values of their reduction potentials. The most abundant and most electropositive metals are in placers (gold, platinum, metals of the platinum group). More electronegative metals - silver and copper - occur less commonly in placers. Metals like lead and tin are very rare and native zinc (most electronegative among native metals) is unique to these settings.

As gold and platinum are most abundant in placers, reductive reactions with cathode precipitation proceed mainly on them. Thus, appearance of exotic mineral concretions is natural (Pt^0 - Pb^0; Sn^0 -Au and others).

The phenomenon of asymmetric precipitation of secondary gold on primary gold grains is explained by the fact that the process of precipitation in the electric current field proceeds only on the cathode side of the electrode conductor.

The electrochemical of mineral genesis has strict "regularities" which leads to the following conclusions:

- new formation minerals of copper, silver, platinum and metals of the platinum group may be expected, which, like gold, can be precipitated on their own primary minerals;

- deposition of these new minerals can be asymmetric where the asymmetry should correspond to the electric field direction;
- if the occurrence native zinc in placers is true, all other electropositive metals (chromium, cadmium, cobalt, nickel, antimony) could also be expected in the metallic form
- since the quantity of metal participating in the reaction (precipitation) is determined according to the second Faraday law, then most new species (minerals) formations might be expected in the most ancient placers and within areas with the highest electric potential gradient;
- these patterns are true not only for gold and platinum placers but also for placers of magnetite, titanium-magnetite and others

Study of these and other observations concerning the processes of mineral genesis in placers will allow estimation the scale of these processes and conditions of their formation

MIGRATION OF METALS AND THEIR ACCUMULATION COMPARED WITH THE CONCENTRATION GRADIENT ("UPHILL" MOVEMENT).

An unexpected effect was noted when working with the method of diffusive extraction (MDE), (Alekseev and Dukhanin, 1989; Alekseev, Goldberg and Dukhanin,1989a, 1989b) The method was intended for use in the search for buried ore deposits According to method capsules made of an electroneutral membrane ("element-collectors"), filled with electrolyte are placed into soil. They are placed for some time and then the solution is analyzed for chemical elements. Accumulation of ions in the capsule solution is often observed in concentrations exceeding their content in the environment, i e an "uphill" movement takes place. The concentration of metal in the "element-collectors" at higher concentrations than the in interstitial solution was considered by us to be due to electric potentials existing on the boundary of the media. This potential was called the "diffusive potential" in Russian geophysical literature (DP), and the associated electric field was named "diffusive electric field" (Semenov,1968) In English geophysical literature this potential was named "liquid-junction electrochemical SP (self-potential) (Sheriff, 1974)

Diffusive potential arises in the earth at the boundaries of rocks of different composition, at the boundaries between layers in rocks of different composition and salinity or concentration differences between underground water and surface groundwater etc The value of diffusive potentials (DP) in the earth accounts for tens and, in some cases even hundreds of millivolts (Semenov, 1968).

- Systems with very high DP values (hundreds millivolts) in the earth arise under extreme condition: on the boundary between highly concentrated acid (>1M) or alkaline solutions and neutral ones (Bischoff et al, 1996)
- Systems with DP values up to tens of mV arise on the boundaries between highly mineralized NaCl, Na_2SO_4 and fresh waters The DP value comes to tens of mV (25-35mV) when the difference in concentrations is 100-1000 times These conditions are typical for geological environments
- Systems with DP of several mV include boundaries between weakly mineralized waters and fresh waters

An "averaging effect" is usually observed in the earth It is characterized both by different coefficients of diffusion and selective sorption of individual ions In Russian geophysical literature such potentials were named diffusive-adsorptive (Semenov, 1968). In English geophysical literature they are known as "shale potential (electrochemical SP)" (Sheriff, 1974) Their values, as follows from field observation, sharply differ from theoretical values calculated by the equation for water solutions As a rule, such potentials are much higher than diffusive potentials and may be equal to hundreds mV

Ion flows, which are moving in rocks in presence of diffusive (diffusive-adsorptive) potentials, are described by the Nernst-Plank equation (Glasstone, 1956, Davies and James, 1976). It takes into account the contribution of the electric field gradient and concentration gradient for transfer of components The geological literature only discusses transfer of components under the influence of concentration gradient. The contribution of the electric field gradients is usually not estimated.

Experimental investigations have been performed to estimate ion concentration under the influence of diffusive potentials

EXPERIMENTAL INVESTIGATIONS.

Ion mass transport processes have been studied in laboratories One common geological system was investigated: a contact between two media of different composition Two solutions of different composition and concentration, divided by a cellophane membrane served as a model of such system A composition and concentration of solutions were selected in order to create electric fields values similar to that occurring naturally (with an absolute value of about 100 mV) Such a diffusive potential (DP - 100mV) was determined by using the Henderson equation on the contact between 0 01 M salt solution KF and 1M HNO_3.

These particular solutions were used for the initial experiments Salt solution was poured into a polyethylene glass; a cellophane capsule with acid solution was place into its center The experiments permitted the study of quantities of components that moved through the membrane during the period of observation To achieve this, the capsule was taken out of the salt solution after a fixed time, cut and solutions from it and from the glass were analyzed for all the elements included in the system In the solutions, concentration of hydrogen ions was determined by titration with sodium hydroxide and methylorange, nitrate ions by the fluorocolorimetric method with a phenol-disulphide acid, potassium ions by flame photometry, and fluorine ions by fluoride-selective ion electrode.

During the experiments, differences in electrical potentials between the investigated solutions were measured with the help of saturated chlorine-silver electrodes DP values on the boundaries between non-polarized electrodes and solution were deduced from this difference The calculations were carried out according to Henderson equation (Davies and James, 1976):

$$pH = 1/2\ pK_W - 1/2\ pK_A - 1/2\ lg\ c$$

Were:

pH - - $lg\ c\ (H^+)$

K_{AW} - constant of ionization of H_2O

K_A - constant of ionization of acid

The resulting values characterized DP between the investigated solutions in the system The initial DP value, arising in the system just after the capsule with acid had been put into the acid solution, was 110 mV. With time, DP values decreased synchronously with equalization of acid concentration either side of the membrane and after 2 hours the difference in electric potential decreased to several millivolts Thus, the chosen model system provided DP life during a limited period of time (2 hours)

Osmotic effects were also observed in the system, manifest as an increase in solution volume in the capsule These effects were not significant because maximum volume increase in the capsule did not exceed 10% of the initial volume

DISCUSSION OF THE RESULTS.

Initially potassium concentration in the inner capsule increases and after 0 5 hours from the beginning of the experiment it becomes higher than the concentration of the ions in the original solution (Fig 3) After three hours the potassium concentration attains a maximum value and then begins to decrease Note that in open natural systems the concentration process is sustained over a long time Fluorine ions diffuse into the capsule at a slower rate than equivalent quantities of potassium ions (Fig 3) Only after 8 hours does concentration of potassium and fluorine ions in the system become equal

The established difference in the behavior of potassium and fluorine ions corresponds to the variation DP The highest rate of potassium ion diffusion is observed at the initial moment when DP is the greatest The rate of potassium ion diffusion decreases with decrease of DP value When the DP value falls to several millivolts, its effect on the mass transfer process becomes negligible and potassium ions diffuse under the influence, of their concentration gradient from the capsule into the surrounding salt solution The dynamics in the of behavior potassium ions can be considered according to Nernst-Plank equation as a result of DP alteration in the system

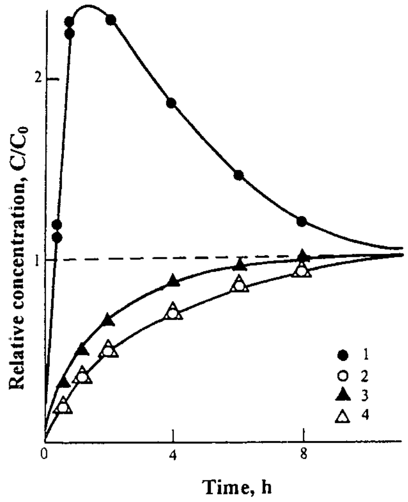

Figure 3: *Change of the relation of concentration ions (potassium and fluorine) in the capsule to concentration into surrounding salt solution by diffuse.*

Potassium - *in nitric acid solution* (1)
in distilled water (2)
Fluorine - *in nitric acid solution* (3)
in distilled water (4)

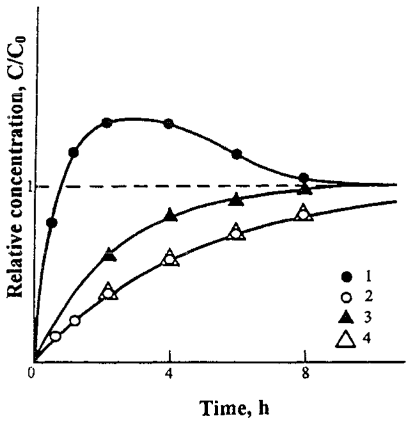

Figure 4: *Change of relation of concentration ions (magnesium and chlorine) in capsule to concentration into surrounding salt solution by diffuse.*

Magnesium - *in nitric acid solution* (1)
in distilled water (2)
Chlorine - *in nitric acid solution* (3)
in distilled water (4)

To confirm the relationship between the electrical field generated and the rate of ion diffusion, the system was modeled where DP values were minimal during the whole experiment. Potassium and fluorine ions were transferred into distilled water. The measured DP values for such a system did not exceed several millivolts. In this case potassium and fluorine ions (Fig.3) diffuse in equivalent quantities (or at a similar rate).

The behavior of magnesium and chlorine ions is similar to that of potassium and fluorine ions during their diffusion from the magnesium chloride solution into the nitric acid solution. Experiments have been performed for the case where DPs at the initial moment are maximum and decrease up to several mV after 2 hours and into distilled water, when DPs during the whole time of the experiment do not exceed several millivolts (Fig 4).

Thus, DPs arising in the system, result in speeding up cation flow relative to anion flow. Electric neutrality of solutions is most likely maintained at the expense of a reduced flow of nitrate ions from the acid solution compared with hydrogen ions.

The results demonstrate the possibility for matter accumulation provided that the boundaries between the different media are kept in non-equilibrium. Such conditions are as a rule maintained in geological environments.

Description of ion diffusion processes versus the gradient of their concentration by Fik's Law (Glasstone, 1956) is impossible for the cases shown in Fig 3 and 4.

Separation of ions according to the sign of their charge can proceed depending on the DP sign with zones of local enrichment. They can arise on the contacts of rocks or natural waters different in composition; it may be especially active near the boundaries between fresh and salt waters and other contrasting media.

FORMATION OF RICH OXIDIZED ORES OF KRIVOROZHSKY TYPE.

Genetic conditions for the formation of the rich oxidized iron ores of the Krivorozhsky type have been discussed for a long time (Belevtsev et al, 1981) There is also no common view on the mechanism for formation of oxidation zones at depths of 2-3km or more, or on the nature of processes responsible for intensive dissolution and removal of quartz, carbonates, silicates on the lone hand and oxidation and retention in place of magnetite (martite) and additional enrichment with iron - on the other At present, the chemical mechanism of these processes is not well understood, because, though it was possible to increase quartz solubility in experiments, the main contradiction - dissolving and removal of quartz and retention of iron (magnetite) under natural conditions - was not solved At the same time, magnetite ore bodies are electrical conductors and it is reasonable to apply electrochemical laws for explanation of their genetic formation.

The deposits of rich iron ore in the Krivirozhsky Basin are significant in size Their thickness may reached 200-240m, they may be 1000-1100m in length ; and extend 3000m down dip In this connection different parts of ore bodies exist in wide interval of physical-chemical conditions These conditions include: variation in ion concentrations of ferrous and ferric iron and other potential-producing ions in the solution associated with irregular distribution of magnetite in ferruginous rocks (Ryss, 1983) From this condtions it follows that occurrence of a galvanic element in the system between ferruginous quartzites and ore is possible

The character of galvanic processes can be estimated based on the composition of rocks and types of reaction proceeding within electrochemical "chain" The chain consists of three parts: anode and cathode (where electrode processes proceed), and intermediate, responsible for ionic processes. Electrochemical studies of every part of the system have been carried out to estimate the role of the galvanic mechanism (Goldberg et al, 1988)

EXPERIMENTAL STUDIES.

Cathode area Study of the processes proceeding on the cathode was performed by cathode polarization of magnetite in a solution of 0 001N NaCl (pH = 5-6). Platinum, placed into another glass, connected with the first one by a salt bridge, served as an additional electrode Content of iron oxides and pH value in this solution were determined Iron content in the solution varied (depending on the duration of the experiments) from 0 4 to 2mg/L

X-ray diffraction analysis of the precipitate revealed two phases: goethite and magnetite. The latter is precipitated on the original magnetite-electrode along the electroneutral edge of the rhombododecahedron The content of ferrous iron in the magnetite lattice increased in the upper layer of the electrode from 24 to 27%

A develop goethite (the complete iron oxide) is produced simultaneously, which contradicts the expected reaction process This contradiction may be explained by the gradation of the process, where electrochemical-reducing reaction is combined with a chemical oxidizing reaction according to the scheme:

$2Fe_3O_4+4e = 6FeO + O_2$ - electrical stage, (1)

$4FeO = Fe_3O_4 + aFe^0$ - decay, (2)

$2aFe^0+1\ 5O_2 = Fe_2O_3$ - chemical stage, (3)

According to Bol, (1962), a Fe^0 (2), produced in chemical process, is stable and it is oxidized at the expense of O_2 (1) to goethite or hematite depending on oxygen abundance of the medium and temperature. This gradated process proceeds on the surface of the electrode and so, secondary magnetite should be precipitated naturally according to the direction of the electric field, and oxidized iron acquires the form of pseudomorphic substitution

Anode area. The study of processes proceeding on the anode was carried out using the same method as for cathode reactions; in this case magnetite was naturally polarized on the anode Experiments lasted from 20 to 130 days without visible changes to magnetite Iron content in solution of anode area increased (from 1 3 to 5 0 mg/l). From 25 to 50% of the soluble iron went into cathode area The pH value in the anode area varied from 6 to 2

Appearance of iron ions in solution points to dissolving of magnetite, but a low pH value prevents iron precipitation near the anode and it is transferred to the cathode area, where it is partially precipitated As a result of such a process the magnetite-anode looks unchanged In more prolonged experiments the sign of magnetite dissolution should clearly appear

The intermediate area corresponds to the outer chain of the galvanic element Here, electrochemical processes proceed on minerals, mainly with ion-covalent bonds (dielectrics and semiconductors) If the rocks contain impregnations and veinlets of ore minerals with electronic conductivity, the cathode-anode processes outlined above will develop on them

The study of processes in ferruginous rock transformation within the electric current field, was carried out in an electrochemical cell (Fig 5) This cell was invented in 1983 (Alekseev, Goldberg and Dukhanin, 1983); This method of concentration of elements was adopted as a principal of both laboratory and field investigation by the CHIM method (Alekseev et al, 1983; Alekseev et al, 1981)

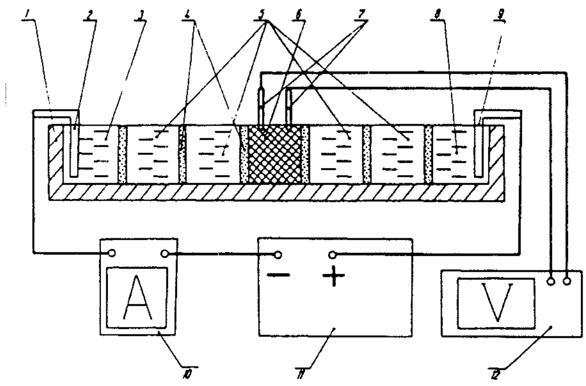

Figure 5: *Electrochemical Nucleus. 1 - Nucleus, 2 & 9 - Platinum electrodes, 3 & 8 - Brim cells, 4 - Parchment membranes, 5 - Intermediate cells, 6 - Central cell, 7 - Non-polarizable measuring electrodes, 10 - Ammeter, 11 - Direct current source, 12 - Voltmeter*

Table 2: *Electrochemical extraction of elements out of carbonate-magnetite quartz*

	MASS OF ELEMENT EXTRACTED OUT OF 1G OF ROCK (MEXT), MKG					
ELEMENT	CATHOLITE	ANOLITE	TOTAL	MASS OF ELEMENT IN 1G OF INITIAL ROCK (M_{INI}), MG	RATE OF EXTRACT MKG/H	DEGREE OF EXTRACT M_{EXT}/M_{INI} x100%
Si	10 1	643.9	654 0	168 9	0.7	0.4
AL	622.0	6 5	628 0	14.2	0.7	4.4
Fe	632 0	2.5	634.0	351.9	0 7	0.2
Ca	4800.0	-	4800 0	12 1	5.3	39 0
Mg	3500.0	10 0	3510.0	16.2	3.8	21.7

The nucleus (1) consisted of the seven cells (3,5,8), which were divided by parchment membranes (4) A pulverized, sieved and moist sample (25g) was placed in the central cell (6) Other cells (5) were filled with a 0.01 N solution of $LiNO_3$

The platinum electrodes (2,9) were located in the outer cells (3,8) and the current switched (10,11,12) on through these electrodes The intermediate cells between the electrodes cells and central cell were used to ensure stable conditions for retention of the metals ions from the central cell It is one of the most efficient of method to impede diffusion of electrolytes from cathode and anode cells

In the central cell, pH was approximately 6-7 It was achieved by means of neutralisation of the hydroxyl ion in the cathode cell by HNO_3 acid and the hydrogen ion in the anode cell by LiOH alkali The concentration of the acid in the cathode cell and the alkali in the anode cell was calculated to take account of the quantity of electricity and mass of the hydrogen and hydroxyl ions, which were created by the electrode processes

Ferruginous quartzite was the object of investigation. Its rock composition is: magnetite - 40%, quartz - 30%, siderite - 30%. Chemical composition of the rock is: $SiO\%^2$ - 36.13%; TiO^2 - 0.06%; $Al_2O\%_3$ - 2.69; $Fe_2O\%_3$ - 25.84; FeO - 22.0%; MnO - 0.3%; MgO -2,7%; CaO - 1.69%; K_2O - 0.2%; Na_2O - 0.18%; S - 0.06%; Pe_2O_5 - 0.03%; H_2O - 0.07%; losses by ignition - 8.54%; S - 100.49%. The 0.1-0.2mm fraction was used in the experiment, its moist was 25%. The experiments were performed at 20oC ± 5 and atmospheric pressure.

The electric field intensity (2 V/cm) was maintained constant in the cell central (6) (fig.5). The average current density was 0.02 A/cm^2. Duration of the experiment was 900 hours. Extraction of various elements out of the rock was observed during the process of the experiments by means of regular (after 40-50 hours) analysis in the cathode and anode cameras. Ca and Mg were determined using Trilon - B; Al, Si, and Fe - using photocolorimetry.

The results of the experiments are shown in Table 2. They indicate that:

- all the enumerated elements are extracted out of rocks electrochemically;
- Si is transported into the anode area and all the other elements - mainly into the cathode area;
- the rate of component extraction is in inverse proportion to their content in the rock;
- according to the degree of extraction the components are arranged in the row (Ca, Mg, Al, Si, Fe) which contrasts to that of their content in the initial rock.

A similar mechanism of dissolution is observed in other rocks as well (Goldberg, 1979). The degree of extraction means that the relationship between the mass of extracted component and its content in the original rock is directly correlated.

DISCUSSION OF THE RESULTS.

The problem of the formation oxidized ores of martite and hematite - martite composition could be described by considering the experimental data.

A geological analogy of the cathode area should be oxidized ores of martite and hematite - martite composition. It may be concluded from the experiments that magnetite ores can be oxidized as a result of the cathode process only at the expense of oxygen in the electrochemical reduction of magnetite. This means that deep zones of oxidation can be formed practically at any depth. In addition to maintenance of iron minerals, they are being enriched at the expense of Fe that is transported into the cathode area and precipitated in the alkaline medium in the form of oxides, hydroxides, and siderite. Simultaneously, silicon ions migrate from this area to an anode area. As a result the content of quartz in the ore bodies decreased or the quartz depletes completely.

In the anode area of Fe and other cations deplete and more Si accumulates. According to the experimental data, the amount of Si accumulation exceeds the amount of depleted Fe, and, as a consequence, dense, cemented silicified rocks will be formed in the anodic part of the system. Another specific feature is the presence of iron only in the form of magnetite. Thus, unlike the cathode, the magnetite-anode is dissolved but stays unchanged as a mineral type.

The intermediate area of the electrochemical chain is characterized by the electrochemical process extraction of Si and Fe. The specific features of this zone are: the dissolution of carbonates and silicates, significant leaching of quartz, martinization of magnetite and its partial dissolution, and, as a consequence of these processes, disintegration of ferruginous quartzites. Spatially, disintegration areas are concentrated around rich ores. This is associated with the smaller size of the cathode area as compared with the anode, which is the reason for the higher current density and, consequently, more intensive electrochemical processes (Ryss,1983). A geological analogy of the above mentioned part of the galvanic sequence may be zones of leached jaspilites - similar to formation of loose quartz bodies in sulphide deposits.

The electrochemical model of rich oxidized (martinite) ore formation, developed from the experimental data, generally corresponds to the geologic structure of ore bodies. The spatial position of the discussed zonality is determined by the structure of a natural galvanic element.

The results from the experiments and average values of natural electric field intensity allow one to estimate the approximate time required for electrochemical transformation of thin-banded ferruginous quartzites and ores resulting in formation of martinite ores with low quartz content. The time can be determined by the equation for electrochemical mass transfer (Goldberg, 1993):

$T = Smi / Ci\ UiESk$

Where:

Smi total quantity of silica, extracted in the process of electrochemical transformation of the rock;
Ci concentration of the electromobile silica form in the matter flow;
Ui mobility of silica;
E electric field intensity;
Sk the area of electric current spreading;
T time of electrochemical extraction

Mass of completely extracted quartz (Smi) was calculated for the following rock volume: length along the strike - 1000m; width - 2000m; thickness - 10cm This volume corresponds approximately to several quartz inter-layers in thin-banded quartz-magnetite quartzites. With these parameters, the total mass of extracted SiO2 should be 5 x 1010g Concentration of the mobile silica form in the solution, according to the above experimental data is 6 x 10-6g/ml, i e close to silica content in underground waters (Levinson, 1974)

Silica mobility during quartz dissolution is taken to be equal to n.10-6 m2/Vh (where n=1-10) based on the experimental data (Goldberg, 1993) Electric field intensity is taken as 10-3V/m Such gradients are common in anomalous areas of natural electric fields (Semenov, 1968), connected with e.m.f type sources of galvanic elements The area of current spreading is determined by the size of the reacting surface of a magnetite electrode If the electrode area is comparable with the quantity of removed SiO2 per a unit of its surface area, then the total surface of the electrode will be 2 x 10-6 m2. But as electric reactions are most active near electrodes, the size of the reacting surface will be only half this Because of this the time for electrochemical removal extraction of quartz is 5 x 108 years. The calculated time does not contradict that defined by the electrochemical model and appears to be reasonable from a geological point of view.

The discussed electrochemical model closely describes the phenomena observed in deposits of the Krivorozhsky type. It may be applied to other deposits of this type associated with Pre-Cambrian deposits of ferruginous quartzites

General Conclusion

Regoliths have been described in many papers and there is much factual material As a rule, interpretation of regolith genesis is done at present without due account of electrical energy. Exceptions are works describing phenomena of oxidation and reduction in sulphide deposits (Sveshnikov,1967; Govett 1973, Shvartzev, 1976, Ryss, 1983) It seems to me that the three examples outlined suggest significant participation of electrical energy and, correspondingly, electrochemical processes in transformation of the geological environment Electrical energy is particularly important in the process of matter concentration In essence, the structure of the electric field itself creates regular areas of dissolution (depletion) and concentration (supply) These processes can move large volumes of rock or develop in local settings according to multi-range character of electric fields

I think that there are two main areas for investigations based on electrochemical phenomena:

- regolith as an object for search for supergene deposits;
- regolith as a model for understanding of processes of matter redistribution, because the system is more accessible for study under near-surface conditions

Experimental data continue to accumulate and methods are being developed which will allow study these of processes by taking into account geoelectrochemistry.

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REFERENCES

Alekseev, S G., Goldberg, I.S., Dukhanin, A S., 1983 . Ustroystvo dlia elektrohimi- cheskogo izuchenia sostava sred Avtorskoe svidetelstvo SSSR # 996983 Bulleten Isobreteniy, 6 (in Russian).

Alekseev, S.G , Dukhanin, A.S., 1989a Diffuzionnoe izvlechenie podvizcgnyh form metallov dlia poiskov skrytogo orudnenia Nauka, Moskow, pp 174- 178 (in Russian)

Alekseev, S G , Goldberg, I.S , Dukhanin, A.S , 1989b. cherez electroneitralnye membrany v pole diffusionnyh potencialov. Zhurnal Fizicheskoy Khimii, 63(9): 2547-2549 (in Russian).

Alekseev, S G , Goldberg, I S , Dukhanin, A S , 1989c Influence of diffusive potentials on the transportation of ions in the earth. Geochemistry, AN USSR, 5: 758-761

Alekseev, S G , Goldberg, I S , Veikher, A A , Gracheva, T R , Dukhanin, A.S , Ivanova, A V 1981 Patterns of electrochemical leaching of elemnts in the simplest physico-chemical systems (Report 1) Selected translation of the Russian literature on the electrochemical sampling techniques called CIHM (Chastichoe Izvlechennnye Metallov) Translator Bloomstein, E , 1900. : Introduction by D B.Hoover and D B Smith U S. Geol Surv Open-File Rep 90-462, 172 pp

Belevtsev, Ia. N , Epatko, Yu. M Verigin, M I I dr., 1981 Zheleznodorozhnye mestorozhdenia dokembria Ukrainy i ih prognoznaia otsenka Kiev, Nayk dumka, 232 pp (in Russian)

Bischoff, J.L , Rosenbaver, R J and Fournier, R O., 1996 The generation of HCl in the system $CaCl_2$ - H_2O: vapor-liquid relations from 380-5000 Geochem Cos-m chim Acta, 60: 7-16.

Bogoslovsky, V A. and Ogilvy, A A., 1972 The study of streaming potentials on fissured media modeles. Geophys. Prospect , 20 (1): 109-117.

Cammann, K , 1979, Working with Ion- Selective Electrodes Chemical Laboratory Practice, 1979. Springel-Verlag, 225 pp

Devies, C W , James, A M ,1976 A dictionary of Electrochemistry The Macmillan Press Ltd , 278 pp

Fittermann, D.,V., Calculations of self-anomalies near vertical contacts. Geophysics, 44(2) pp.195-205

Giblin, A , 1997. Geochemistry of Groundwaters in the Vicinity of Stawell, Clunes, Arrowroot and Ballarat Gold Deposits. The AusIMM Annual Conference, Ballarat, 181-191pp.

Glasstone, S , 1956. Textbook of physical chemistry, Second edition, 1319 pp

Goldberg, I S , 1979. Electrogeochemical extraction of elements from rock. ONTI VITR, 127: 59-66 (in Russian).

Goldberg, I S , Basko, T V , Voronin, D B., Epatko, Y M., 1988. O vozmozhnoy roli Elektrohimicheskih processov v obrazovanii okiclennyh rud krivorozhckogo tipa. Geologicheskii zhurna l,6 Kiev, pp 11-15 (in Russian)

Goldberg, I S , 1993 Geoelectrohimicheskie izvlechenia elementov iz porod ienergii rudoobrazovanii. St Petersburg, NPO Rudgeofizika, "Safronov's reading", pp 135-151 (in Russian)

Govett, G J S , 1973. Differential secondary dispersion in transported soils and post-mineralisation rocks: an electrochemical interpretation London symposium,Vol pp 81-91

Iabloneva, S B , 1965 Geologiia rossypey. Moskva, Nauka, 350 pp (in Russian)

Keller, G V ,and Frischknecht, F C , Electrical Methods in Geophysical Prospecting, Pergamon Press, 519 pp

Kinory, S , Nakabyshi, K and Shibato, K , 1955 A review of origins of thegeneration of SP current Geophysical exploration of deposits, 6(3-4): 227-235

Levinson ,A A , 1974 Introdaktion to Exploretion Geochemistry Second edition, 929 pp

Ryss,Y.S ,1983 Geoelektrochimicheskie metody razvedki Leningrad, Nedra, 255 pp (in Russian)

Safronov, N I , Mescheriakov, S S , Ivanov, N P., 1978 Energia rudoobrazovania. Leningrad, Nedra, 212 pp (in Russian)

Schiavone, D and Quarto, R , 1984. Self-potential prospecting in the study of water movements Geoexploration, 22, pp 47-58 S

Semenov, A S ,1968 Elektrorazvedka metodom estestbennogo elektricheskogo polia Leningrad, Nedra, 447pp (in Russian)

Sheriff, R E., 1974 Encyclopedic dictionary of exploration geophysics Tulsa, Oklahoma, Society of Exploration Geophysicists, 190 pp.

Shvartsev, S L., 1976 Electrochemical dissolution of sulphide ores J Geochem Explor.,5: 71-72

Smith, R E, 1996 Regolith research in support of mineral exploration in Australia J Geochem. Explor., 57: 159-173

Sveshnikov, G B., 1967 Elektrohimicheskie processy na sulfidnyh mestorozhdeniiah

Leningrad, Isdatelstvo Leningradskogo Universiteta 160 pp (in Russian).

Vernadskiy, V I, 1955 Izbrannye sochineniia T 2, 695 pp (in Russian)

Voronin, D B, Goldberg, I S., 1972 Electrochemical processes in placer deposits of native elements AN USSR, V 2, 1: pp 190-192.