

Hydrothermal equilibria and ore formation

Alekhin Y.V., Fyayzullina R.V. The main valence mercury forms equilibria in the two-phase fluids

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Abstract. Despite the abundance of work, including on the thermodynamic properties of forms transport of mercury, some fundamental aspects of its mezhrezervuarnogo exchange remained in the shadows. Our practice of sampling and analysis of atmospheric samples and natural samples of two-phase fluids in the areas of development of modern gas-steam term showed that the solid and liquid aerosol form can be attributed only 1–3% of the mercury. The overwhelming part is present as a highly volatile, dynamic levels of concentration of the gas mixture forms, as well as mercury, dissolved in water drops. There was a mysterious mechanism of the famous paradox of rapid leaching of mercury from the atmosphere during torrential rains, as we had previously been specifically shown that water vapor does not react with atomic vapors of elemental mercury, forming an ideal gas mixture. How, then, after a period of accumulation of mercury in dry air, is almost complete washout from the atmosphere within a few hours, with a decrease in concentration in the tens to hundreds of times before the usual background level of 1.5 ng/m³, is characteristic of the air over the oceans and even lower? On the part of the amount of signs clearly did not suit us studied form Hg⁰. If the gas phase can accumulate atomic mercury vapor to high levels of concentration (600 ng/m³), it is unclear what happens to them in the humid air and the appearance of drops of water? The same question arises for two-phase fluids combined cycle term. Analysis of our data explains a number of contradictions in the numerous observations of the dynamics of changes in the concentrations of mercury in therms of Kamchatka, and in the air. 550.426: 550.4.2: 550.41

Keywords: solubility and vapor pressure of HgO, solubility of Hg⁰, Henry's constants.

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Earlier we (Alekhin et al., 2003; Mukhamadiyarova (Fyayzullina), 2012) studied the hydration of mercury vapor in the gas-vapor phase Hg⁰–H₂O system at 180°C. This temperature is not only quite close to the maximum temperature of formation of mercury deposits, ie Transfer characterizes the conditions of its forms, but also, according to our latest data (Alekhin, Fyayzullina, 2015), corresponds to the region of dominance in the gas-vapor phase is vapor Hg⁰. The main issue to be solved in such experiments hydrated whether couples, such as elemental mercury vapor water. If this process is quantitatively significant, it should influence the evaluation of solubility in the gas phase and the magnitude of the transfer in the gas-vapor phase, in the form of hydrated molecular complexes (Alekhin, Vakulenko, 1987). Evaporated during the experiments the amount of mercury originally was

determined by the mass loss microdroplets (Table 1). Use scales that detect mass deficit to within 10⁻⁶ g. A number of studies and complex solubility in water vapor has been shown (Alekhin, Vakulenko, 1987; Vakulenko et al., 1990; Alehin et al., 1994), that the dependence of the mole fraction of the dominant form of the dissolved complex hydrate by the vapor pressure of water as a complexing agent defined by the formula: $d \lg X_{\text{Hg}(0)} / d \lg p = n - 1$, where n - the number of hydrate, $X_{\text{Hg}(0)}$ - the mole fraction of Hg⁰ in the gas phase. In the case of non-hydratable forms of gas ($n = 0$), the slope of the graph $\lg X - \lg p$ is equal to 1, and the limit value in the $\lg p X_{\text{Hg}(0)} = 1$ must comply with the vapor pressure of pure condensed phase component (Fig. 1). This prediction is in the previously studied systems with complexes volatility compounds, we were not detected (typically, $n = 1-4$). But in this system in all cases, the amounts of mercury vapor, vaporized in a very different autoclave volumes (Table 1) sufficiently closely match its partial pressure above the liquid mercury (which is the saturated vapor pressure at the chosen temperature and pressure variables of water vapor). Approximated by the vapor pressure of mercury at $\lg X = 0$ ($\lg p = -2.00$) differs slightly from the well tabulated values Hg⁰ vapor pressure at 180°C ($\lg p = -1.93$) in the regional system, that is, the case illustrates the ideal mixing without chemical interaction and without the formation of hydrate complexes in the gas phase (Fig. 1).

The result, with the apparent hydrophobicity of elemental mercury, was predictable, but left unresolved the problem of rapid washout of its vapor from the atmosphere when torrential rains (Pleijel, Munthe, 1995; Schroeder et al., 1998; Steffen et al., 2005), which is always marked and us (Mukhamadiyarova et al., 2008; Mukhamadiyarova, 2011). We also (Alekhin et al., 2007; Alekhin et al., 2009; Mukhamadiyarova 2011; Fyayzullina, Alekhin, 2015; Alekhin, Fyayzullina, 2015), followed by other authors (Ozerov, 1986; Ozerova et al., 1988; Sorokhin et al., 1978; 1988) noted hurricane gross mercury content in some terms Kamchatka gas-steam, especially in two-phase fluids. Calculations show that such levels of concentration in the gas-vapor mixture and their condensates can not be explained only in pairs its elemental form, especially given our recent data on the solubility in water under reducing conditions, the Henry's constant Hg⁰ (Alekhin et al., 2011₁; Alekhin et al., 2011₂; Alekhin et al., 2011₃).

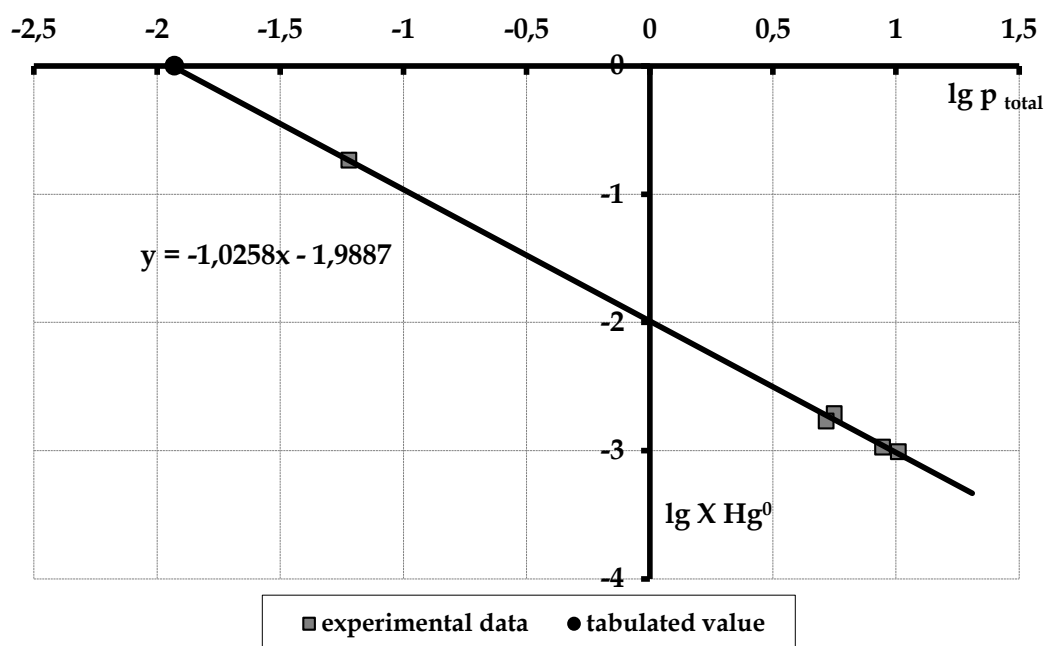


Fig. 1. The dependence of the mole fraction of the total mercury in the gas phase pressure system $\text{Hg}^0\text{--H}_2\text{O--O}_2$ при 180°C.

Table 1. The results of determination of mercury vapor from the microdroplets in the volume autoclave at 180°C

№	$V_{\text{autoclave}}, \text{cm}^3$	$\Delta m_{\text{Hg}(0)}, \text{г}$	$\Delta m_{\text{H}_2\text{O}}, \text{г}$	$p_{\text{H}_2\text{O}}, \text{бар}$	X_{Hg^0}	$\lg X_{\text{Hg}^0}$	$\lg p_{\text{H}_2\text{O}}$
1	3.1	0.000165	0.40144	8.81	0.001064	-2.97	0.94
2	3.1	0.000178	0.34233	10.21	0.000979	-3.01	1.01
3	8.4	0.001518	0	0.049	0.184273	-0.73	-1.31
4	37.8	0.002277	0.64817	5.6	0.001942	-2.71	0.75
5	36.64	0.001784	0.69938	5.2	0.001695	-2.77	0.72

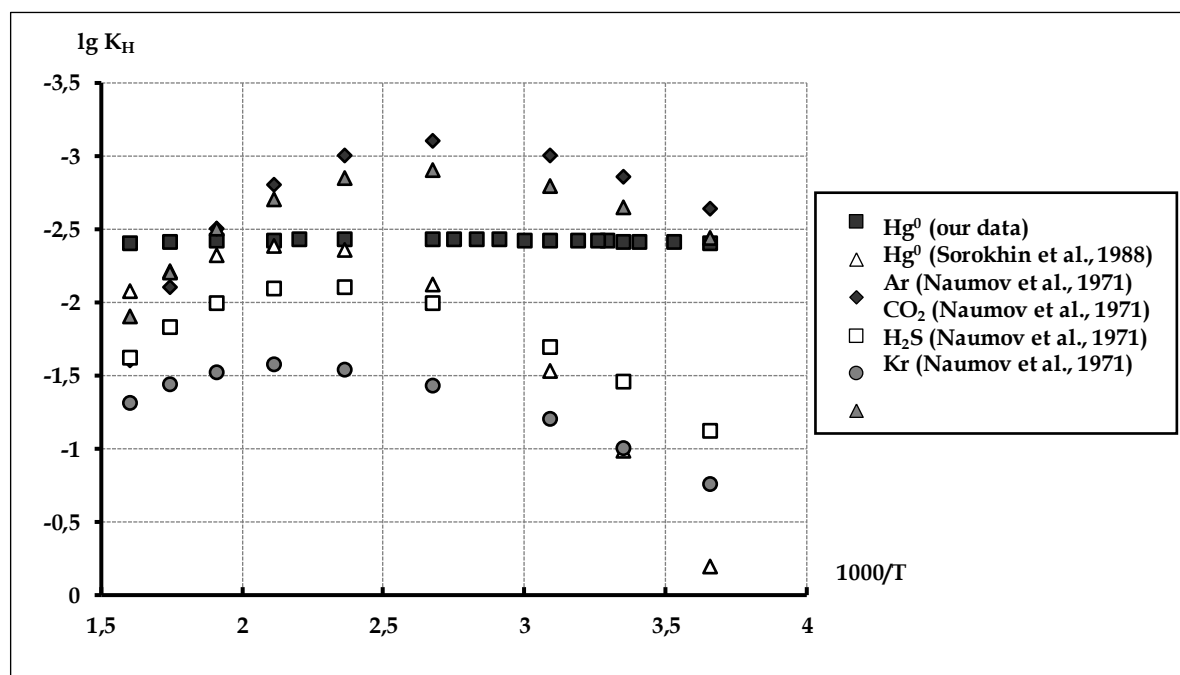


Fig. 2. Dependence of the Henry's law constant of $1/T$ for different gases and vapors Hg^0 .

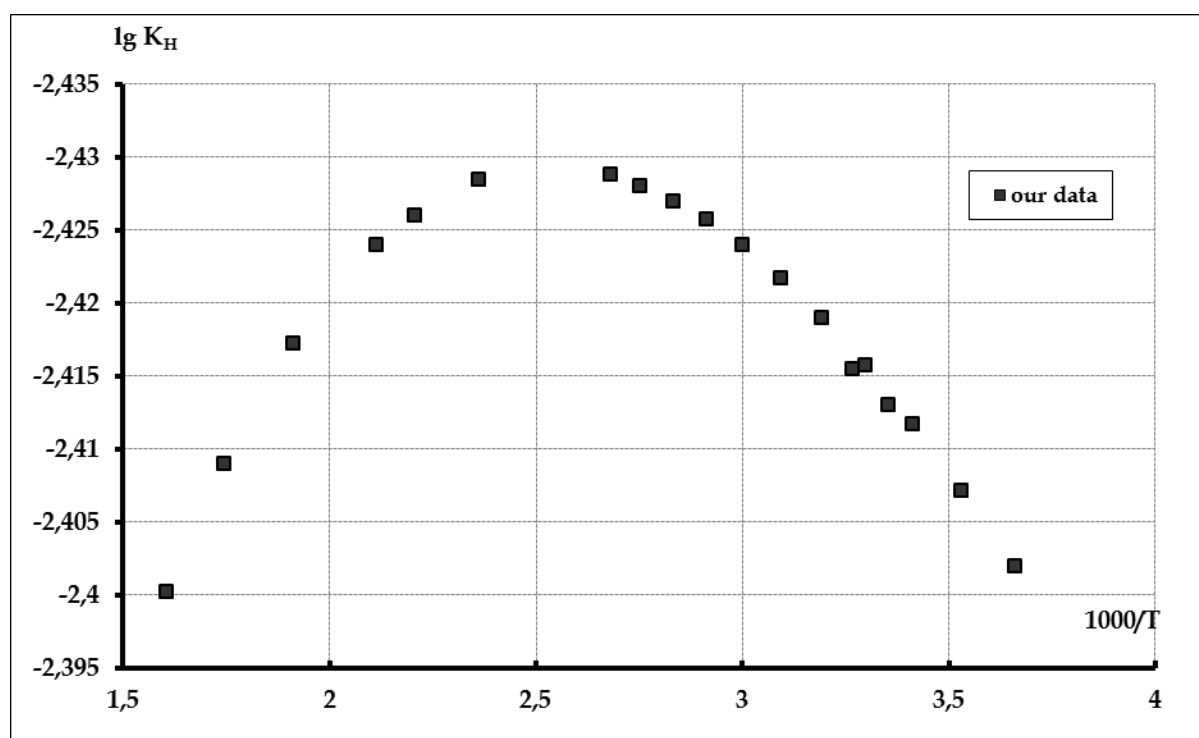


Fig. 3. Extremity Henry constant Hg^0 $1/T$ coordinates detailed in our data.

These results, but with a few large errors were confirmed in experiments at 90°C isotherm. Thus, it was shown that in the system $Hg^0-H_2O-O_2$ with dry steam to 180°C and such experimental conditions (oxygen fugacity close to standard atmospheric) no significant hydration and solubility in the gas phase wholly corresponds to the partial vapor pressure of atomically mercury.

The results of determining the solubility of mercury in the form $Hg^0_{(aq)}$ challenged us to adjust the value of the Henry's constants for a wide range of temperatures and in view of our literature. It is well known that the process of dissolution of inert gas and slabogidratiruemyh water temperature dependence of the Henry's constants extreme (Naumov et al., 1971). In Figure 2, we applied some of the data of the work (2), our data as well as data Sorokhin VI (Sorokhin et al., 1988) in Hg^0 and, for comparison – the data for such well hydratable gases as CO_2 and H_2S . Attention is drawn to the following facts: 1) the value of our little closer to the solubility of inert gases (Ar, Kr) and categorically different from both Sorokhin data and data on acid gases; 2) on this scale we have not seen the temperature extremality we obtained values of the Henry's constants, that was amazing.

Therefore, the results obtained by our precision values of the Henry's constants were separately reconstructed a detailed scale (Fig. 3), which has revealed a distinct, very characteristic extrema in the temperature range of 120-130°C, close to the position of the extrema in systems with noble gases (Ar, Kr).

Despite the abundance of (Ozerova, 1986), including our (Alehin et al., 1987; Alekhin et al., 2009; Alehin et al., 2011), according to the forms of mercury transport, their thermodynamic properties (Ozerova et al., 1988; TKB database; Gorbacheva, 1998; Rusin, 1998; Kazenas, Tsvetkov, 2008; Alekhin et al., 1992; L'vov, 1999), some fundamental aspects of its between reservoirs exchange (Alekhin et al., 2010; Mukhamadiyarova, 2011, 2012) remained in the shadows. Practice sampling and analysis of atmospheric samples and natural samples of two-phase fluids in the areas of development of modern gas-steam term indicates that the solid and liquid aerosol form can be linked only 1–3% of the mercury. The main part of the present as a very volatile, dynamic levels of concentration of the gas mixture forms as well as forms of mercury dissolved in a drip-liquid water. There was a mysterious mechanism of the famous paradox of rapid leaching of mercury from the atmosphere during torrential rains, as we have previously shown to specifically (Alekhin et al., 2003; Mukhamadiyarova (Fyayzullina), 2012), that water vapor does not react with elemental mercury atomic pairs, forming an ideal gas mixture, and the solubility of this form of mercury Hg^0 , liquid water is extremely low (less than $10^{-8} m$) even at equilibrium saturation liquid mercury. Fig. 4 shows experimental data on the so-called "soluble liquid mercury" in the (Sorokhin et al., 1988), along with our recent results (Alekhin et al., 2011).

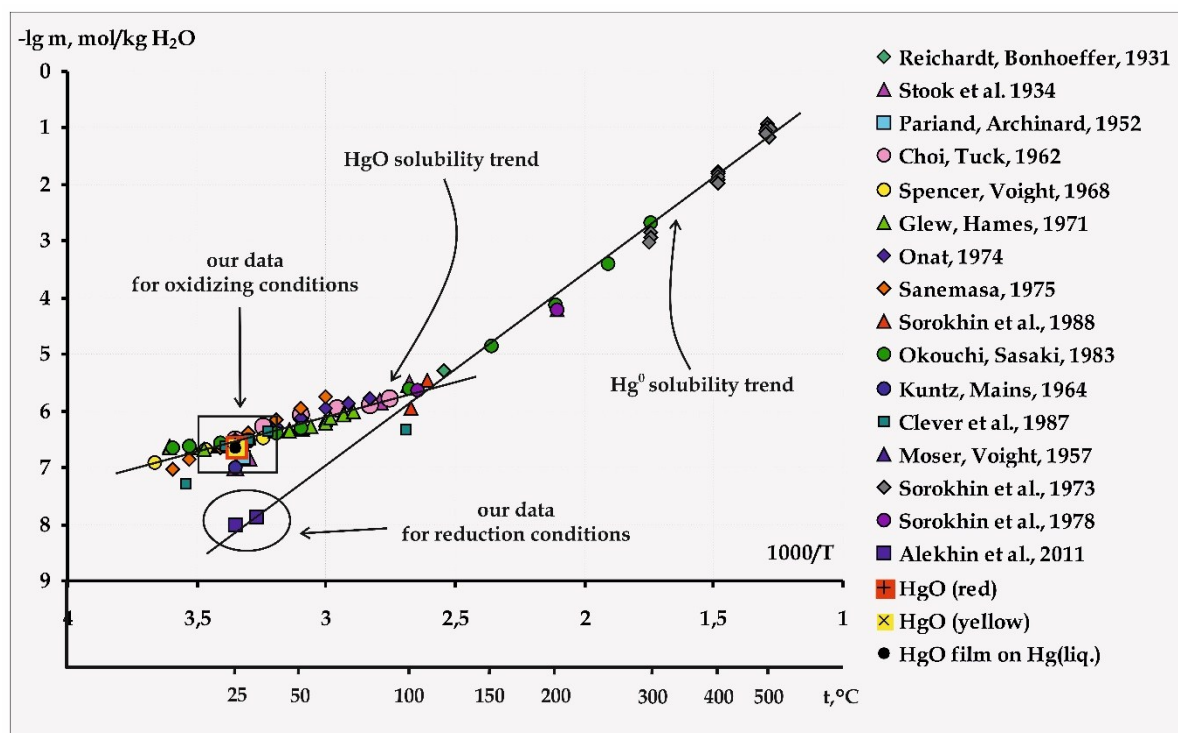


Fig. 4. Data on the of the joint solubility Hg⁰ (aq) and HgO at various temperatures

A modern interpretation of these results shows why, after long periods of (Alekhin et al., 2010; Mukhamadiyarova, 2011, 2012), the accumulation of mercury in dry air, it occurs almost complete washout from the atmosphere for several hours. On the part of the amount of signs clearly not good shape Hg⁰_{aq}. As the only one studied earlier (Alekhin et al., 2011₁; Alekhin et al., 2011₂; Alekhin et al., 2011₃). A similar situation according to our observations is typical for two-phase fluid of steam and gas fluids. In the analysis of liquid condensates, we (Alekhin et al., 2009; Mukhamadiyarova, 2011, 2012; Fyayzullina, Alekhin, 2015; Alekhin, Fyayzullina, 2015) followed by other authors (Ozerova, 1986; Ozerova et al., 1988), we noted hurricane mercury concentrations, but the monitoring of the direct determination of the content in the gas phase over terms here, in the place marked a concentration close to the background of the atmosphere. It is noteworthy that these two objects – atmospheric condensates and condensates thermal jets always weakly mineralized and unlikely to contribute to other systems, such as chloride (Sorokhin et al., 1978). Thus delivery to the deep mercury gas stream usually is beyond doubt, and the aqueous liquid phase often occurs either during the condensation of atmospheric water vapor, or earlier stage of interaction of relatively dry gas streams when bubbling through the water surface horizons. The two-phase fluid systems present oxidized form of HgO_(g), it is then accumulated in the liquid aqueous phase. Heterophasic equilibrium with this second form in atomic vapor Hg (Alekhin, Fyayzullina, 2015) to be very labile in the presence

of water and in anhydrous system inhibited. That such behavior is characterized by a pair of HgO. It remained to prove it that is to confirm the calculation of the appropriate balance. Oxide of mercury (II) may form in the water directly in contact with liquid mercury, in spite of its position in the electrochemical series of metals (Remy, 1974), but according to our data (Mukhamadiyarova, 2012), the kinetics of the oxidation through the aqueous phase by the reaction $\text{Hg}^0_{(\text{liq.})} + 0.5 \text{O}_{2(\text{g})} = \text{HgO}_{(\text{aq.})}$ is quite slow due to the diffusion limitations. This is not the gas-forming reaction of the elements or thermal dissociation phase HgO_(s), for which the decomposition kinetics is well understood not only by mass spectrometry of gas effusion (Kazenas, Tsvetkov, 2008), and other methods (L'vov, 1999). In general, the decomposition reaction of the heterophasic montroidit scheme: $\text{HgO}_{(\text{s})} = \text{Hg}^0_{(\text{g})} + 0.5 \text{O}_{2(\text{g})}$ in the system studied HgO–Hg⁰ sufficiently long and well (Taylor, Hullet, 1913; Taylor, 1962; Kazenas, Tsvetkov, 2008; Rusin, 1998; Gorbacheva, 1998), but we should first of all is interested in gas-homogeneous reaction in the presence of oxygen: $\text{HgO}_{(\text{g})} = \text{Hg}_{(\text{g})} + 0.5 \text{O}_{2(\text{g})}$, and the possible implications for the type of heterogeneous equilibria: $\text{Hg}^0_{(\text{g})} + \text{HgO}_{(\text{g})} + \text{H}_2\text{O} = \text{Hg}_2^{2+} + 2\text{OH}^-$. For a reaction to form a red crystalline phase montroidita enthalpy of its formation elements is relatively small (–21.7 kcal/mol), i.e. is the same (21.7 kcal/mol) and heat of dissociation into elements substantially phase state, there is little evidence of mercury affinity to oxygen and its particular kinetics of the oxidation mechanism. Furthermore, dry air is mercury

oxidation at an appreciable rate only at temperatures close to the boiling point $\text{Hg}^0_{(\text{liq.})}$ (Remy, 1974; Kazenas Tsvetkov, 2008), which once again shows the boundary position of the metal in a number of standard voltages hydrogen right next to precious metals. It is the presence of water initiates a reaction of oxidation and dissolution of the resulting molecule $\text{HgO}_{(\text{g})}$ the reactions $\text{Hg}^0_{(\text{g})} + \text{HgO}_{(\text{g})} + \text{H}_2\text{O} = \text{Hg}^{2+}_2 + 2\text{OH}^-$ and $\text{HgO}_{(\text{g})} + \text{H}_2\text{O} = \text{Hg}^{2+} + 2\text{OH}^-$.

Below is a main objective of the settlement of the latest experimental data to show what conclusions one can come to equilibrium valent forms in the air and on the distribution of the dominant forms of mercury in the liquid and gas phases of two-phase thermal fluids, using data on the equilibrium vapor over $\text{Hg}^0_{(\text{g})}$ and $\text{HgO}_{(\text{g})}$. Montroidit Solubility in water ($\text{HgO}_{(\text{s})}$) is sufficiently high (51.282 mg/kg H_2O or $2.37 \cdot 10^{-7}$ mol/kg at 298.15 K) and significantly higher solubility of elemental mercury in water under these conditions (Alehin et al., 2011) (1.95 mg/kg H_2O or $9.72 \cdot 10^{-9}$ mol/kg). For labile equilibrium in the presence of water $\text{Hg}^0_{(\text{g})} + \text{HgO}_{(\text{g})} + \text{H}_2\text{O} = \text{Hg}^{2+}_2 + 2\text{OH}^-$ a concentration ratio in the aqueous phase ($\lg m_{\text{Hg}(0)} = -8.01$ and $\lg m_{\text{HgO}} = -6.63$), and as a result the redox process heterophasic disproportionation (Alekhin et al., 1992) can detect prompt washout highly soluble oxidized form of the gas phase.

For a homogeneous gas reaction $\text{HgO}_{(\text{g})} = \text{Hg}^0_{(\text{g})} + 0.5 \text{O}_{2(\text{g})}$ for a range of 0–100°C calculations were performed under the following conditions: $C_p^0(T)_{\text{Hg}(0)(\text{r})} = \text{const} = 4.968$ u.h.c. that is common to all monatomic gases, without, by analogy with inert gases (database TCS), rotational and vibrational degrees of freedom. For $\text{O}_{2(\text{g})}$ for $C_p^0(T)$ used a three-parameter equation $C_p = a + b \cdot T + c \cdot T^2$, where $a = 7.16$; $b = 1.00 \cdot 10^{-3}$; $c = -0.40 \cdot 10^5$ (Naumov et al., 1971). Somewhat more complicated was a question in relation to the value of $C_p^0(T)$ for a particle $\text{HgO}_{(\text{g})}$, as reference data on the enthalpy of the particles are contradictory (database TCS; Karpov et al., 1968). By using Shomate's coefficients (Borisov, Shvarov, 1992; Chase, 1998) and from the detailed polynomial in T , using the value obtained $C_p^0(298.15) = 7.81$ u.h.c. (Chase, 1998) for the temperature range of 0–100°C, we received good experimental data

describing two-parameter equation of the heat capacity of particles $\text{HgO}_{(\text{g})}$ $C_p^0(298.15) = 6.16 + 5.53 \cdot 10^{-3}$. Hence, for a homogeneous gas reaction $\text{HgO}_{(\text{g})} = \text{Hg}^0_{(\text{g})} + 0.5 \text{O}_{2(\text{g})}$ an equation for $\Delta_r C_p(T)$: $\Delta_r C_p(T) = 2.384 - 5.03 \cdot 10^{-3} \cdot T - 0.20 \cdot 10^5 \cdot T^{-2}$ with constant integration at 298.15 K:

$$\begin{aligned} x &= \Delta H^0_{298.15} - \Delta a \cdot 298.15 - 0.5 \Delta b \cdot (298.15)^2 + \Delta c \cdot (298.15)^{-1}; \\ y &= \Delta S^0_{298.15} - \Delta a \cdot \ln 298.15 - \Delta b \cdot 298.15 + 0.5 \Delta c \cdot (298.15)^{-2}; \\ \Delta G^0_T &= x + (\Delta a - y) \cdot T - \Delta a \cdot T \cdot \ln T - 0.5 \Delta b \cdot T^2 - 0.5 \Delta c \cdot T^{-1}. \end{aligned}$$

As a result of this temperature range, obtained by a simple and workable equation:

$$\begin{aligned} \Delta G^0_T &= \\ 4122.89 &+ (2.38 + 2.69)T - 2.38T \cdot \ln T + 0.5 \cdot 5.03 \cdot 10^{-3} \cdot T^2 + \\ &+ 0.5 \cdot 0.1 \cdot 10^5 \cdot T^{-1}. \end{aligned}$$

The analysis is limited to temperatures: 273.15; 298.15 and 373.15, and estimate the ratio of volatilities $\text{Hg}^0_{(\text{g})}/\text{HgO}_{(\text{g})}$ first for the case of the partial pressure of oxygen in the atmosphere $f_{\text{O}_2} = 0.2$. For 273.15 K $\lg K = 1.6534$, that in the case of $0.5 \lg f_{\text{O}_2} = -0.345$, resulting in:

$\lg f_{\text{Hg}(0)(\text{g})} - \lg f_{\text{HgO}(\text{g})} = -1.6534 + 0.345 = -1.3074$. It follows that the ratio of volatilities of these gas forms $f_{\text{Hg}(0)(\text{g})}/f_{\text{HgO}(\text{g})} = 0.0492$, i.e. Only 4.92% of the amount of mercury-containing gas is represented by $\text{HgO}(\text{g})$ in an atmospheric air at these conditions.

Similarly, to 298.15 K, $\Delta_r G^0 = 1.83$ kcal / mol and $\lg K = -1.343$, and the ratio of volatilities, $f_{\text{Hg}(0)(\text{g})}/f_{\text{HgO}(\text{g})} = 0.10$ (10% $\text{HgO}(\text{g})$ and 90% $\text{HgO}(\text{g})$). Somewhat more complicated calculations to 373.15 K, when necessary accounting vapor pressure of water, but $\lg f_{\text{Hg}(0)(\text{g})} - \lg f_{\text{HgO}(\text{g})} = -0.6554 + 0.345 = -0.3104$. For the (first) case of dry steam $f_{\text{Hg}(0)(\text{g})}/f_{\text{HgO}(\text{g})} = 0.489$ (32.9% $\text{Hg}^0_{(\text{g})}$). However, if $f_{\text{H}_2\text{O}} = 0.9$ bar, and stored characteristic relative content of atmospheric gases, ie, already $f_{\text{O}_2} \neq 0.2$ ($f_{\text{O}_2} = 0.02$ and $0.5 \lg f_{\text{O}_2} = -0.849$). In this case, $\lg f_{\text{Hg}(0)(\text{g})} - \lg f_{\text{HgO}(\text{g})} = -0.6554 + 0.849 = 0.194$; and the ratio $f_{\text{Hg}(0)(\text{g})}/f_{\text{HgO}(\text{g})} = 1.563$, and the proportion of vapor $\text{HgO}(\text{g})$ in a mixture of mercury emissions to be close to 61%. Then 100°C isotherm, at variable f_{O_2} (Table 2):

Table 2. Ratio vapor $\text{Hg}^0_{(\text{g})}$ in a mixture of gases containing mercury at 100°C (with $f_{\text{H}_2\text{O}} = 0.9$ bar)

f_{O_2}	0.1	0.02	0.01	0.001	0.0001	0.00001
$\text{Hg}^0_{(\text{g})}$, %mol.	41.1	61.0	68.9	87.5	95.7	98.6

Computing values for variables oxygen fugacity in hydrothermal systems and air at different temperatures can be performed using the equation for equilibrium The provided valence forms of mercury in view of the total pressure and water vapor pressure. For the interval of heights it is more

convenient to describe the ratio of volatilities $\text{O}_{2(\text{g})}$, $\text{Hg}^0_{(\text{g})}$, $\text{HgO}_{(\text{g})}$ and $\text{H}_2\text{O}_{(\text{g})}$.

These highly labile and reversible reactions lie in the basis of the dual behavior of mercury vapor-gas two-phase fluids: combination of high elasticity atomic mercury vapor with their chemical inertness and low solubility in water, on the one hand, and

relatively high solubility of HgO. Consideration of our data and literature data (field and experimental) on the composition of the coexisting fluid phases relieves a number of previously unexplained contradictions in the numerous observations of the dynamics of changes of mercury concentration in the coexisting phases of the Thermae of Kamchatka and in the air.

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Zakirov¹ I.V., Suvorova¹ V.A., Aranovich² L.Ja. New data on gold solubility in the steam phase of H₂O-Na₂CO₃ system at increased temperature and pressure

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Abstract. We report results of experimental measurements of gold concentration in steam phase (liquid, vapor or supercritical fluid, depending on the experiment *P-T* and starting Na₂CO₃ composition) saturated with solid Na₂CO₃ in the binary H₂O-Na₂CO₃ system. Experiments have been made in a wide range of compositions of initial solutions at temperature 300÷500°C and pressure 23÷60 MPa. Gold solubility goes down with increase of pressure and increases with temperature in the studied *P-T* range.

Key words: solubility of gold, the steam phase, elevated temperature and pressure.

Citation: Zakirov I.V., V.A. Suvorova, L.Ja. Aranovich. 2015. New data on gold solubility in the steam phase of H₂O-Na₂CO₃ system at increased temperature and pressure. *Experimental Geochemistry*. V. 3. N 4. Pp.

http://exp-geochem.en/JPdf/2015/04/Zakirov_en.pdf

It is known [Lafon, Demazeau, 1994] that quartz is well dissolved in alkaline solutions, and its solubility in Na₂CO₃ solutions is higher than in NaOH. The typical vein association of gold with quartz allows assuming that silicon dioxide and gold are transferred in common in the alkaline environment. For verification of this assumption we made a series of experiments on determination of gold solubility in Na₂CO₃ solutions.

Earlier experiments on studying gold solubility were made in the temperature range 350÷500°C and pressure from 23 to 60 MPa by the technique used when studying solubility of Na₂CO₃ [Zakirov, Suvorova, Aranovich, 2013]. The initial composition of the solution corresponded to 0.05, 0.1 and 0.2M of Na₂CO₃.

In this work the behavior of gold was also investigated in vapour of 0.25M Na₂CO₃ solution on the experimental unit allowing selecting test of steam in the experimental mode [Zakirov, Sretenskaya, 1994, Zakirov et al., 2007]. Regulation, measurement and record of temperature and pressure in it were carried out by means of specially developed interface. That was in turn connected to the computer, the block of tiristors, sensors of pressure and thermocouples. Experiments were carried out with strongly alkaline solutions (pH initial solution = 10.6÷12.2). Therefore the unit was modified: a new combination of materials of the reactor and an internal ampoule for selection of a steam phase portion was used. Besides new materials of units and seals of the unit providing its tightness and stability in strongly alkaline environments peculiar to carbonate solutions were picked up.

For achievement of equilibrium the system was kept at the constant mode not less than a day; then the ampoule with steam and reagents dissolved in it was locked and the autoclave was cooled with flowing water. The volatility of oxygen *f*O₂ in experiments was controlled; the structure of the Ni-NiO buffer before and after specially performed experiments according to XRD data remained invariable. It should be noted that autoclave material

Hydrothermal equilibria and ore formation

(EP-437 alloy) creates fO_2 close to that which creates the Ni-NiO buffer.

Results of experiences are presented in figures 1÷8.

The dispersion of points on isotherms of figures 1÷4 is considerable, especially at 450°C. Nevertheless, it is rather clearly seen that solubility

of gold decreases with pressure for all the studied values of concentration of the initial solution.

Character of the dependence of the gold content on temperature is complex. Gold solubility grows in concentrated solutions with increasing temperature within all the pressure range (figures 5÷7).

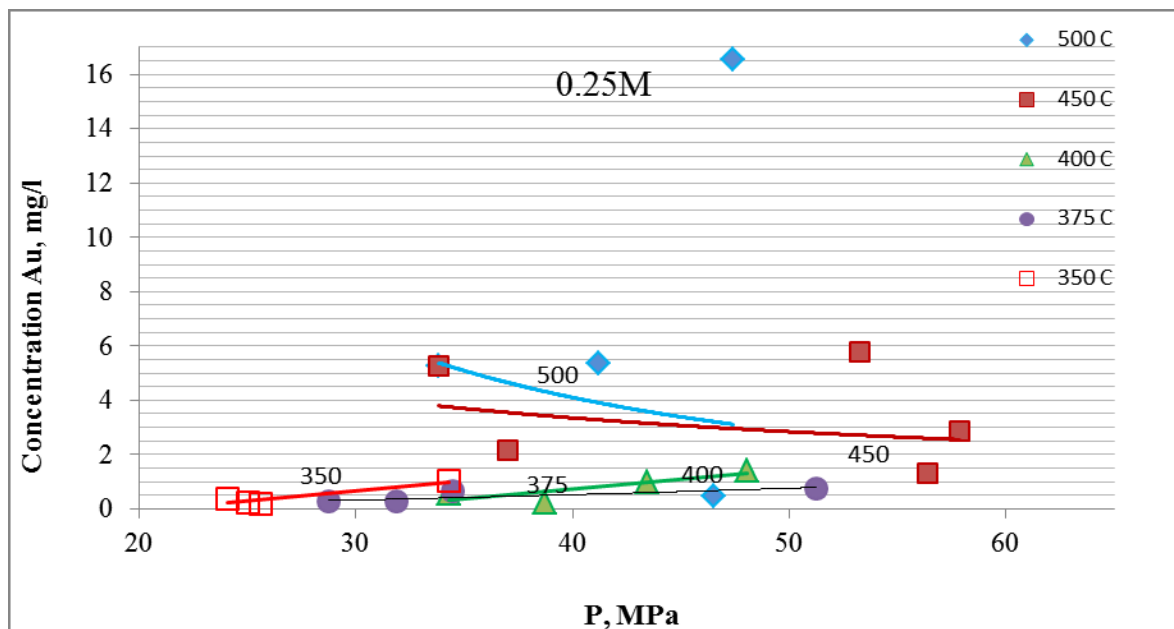


Fig. 1. Pressure dependence of Au content in the steam of 0.25M Na_2CO_3 solution in the temperature range 350÷500°C

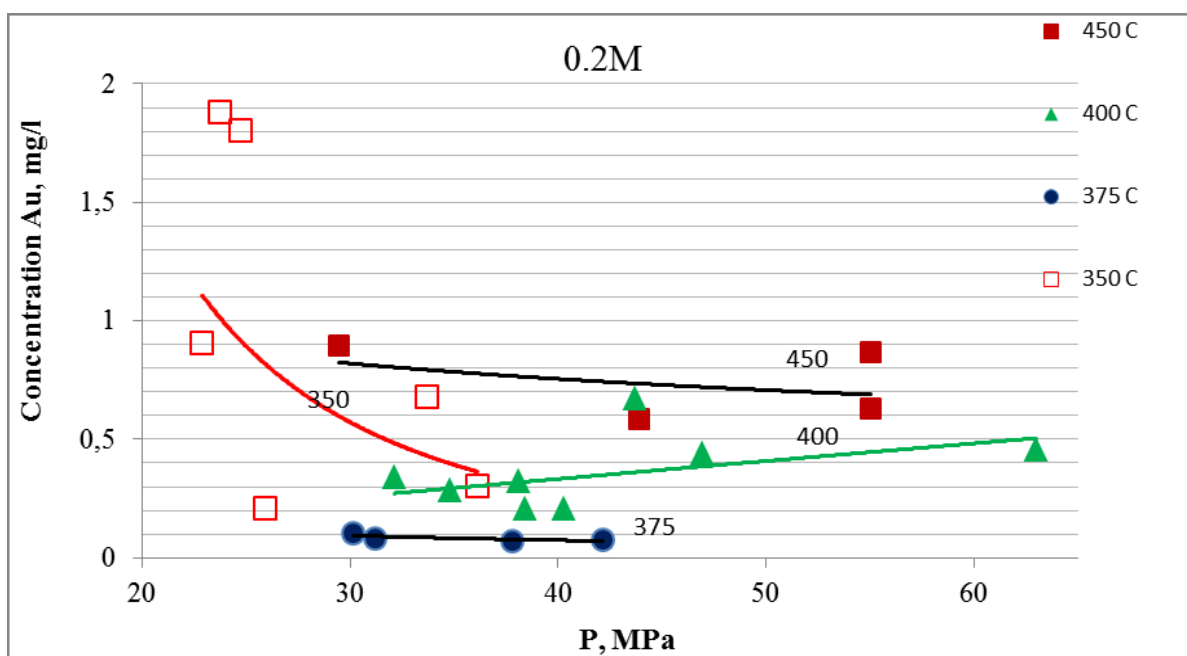


Fig. 2. Pressure dependence of Au content in the steam of 0.2M Na_2CO_3 solution in the temperature range 350÷500°C.

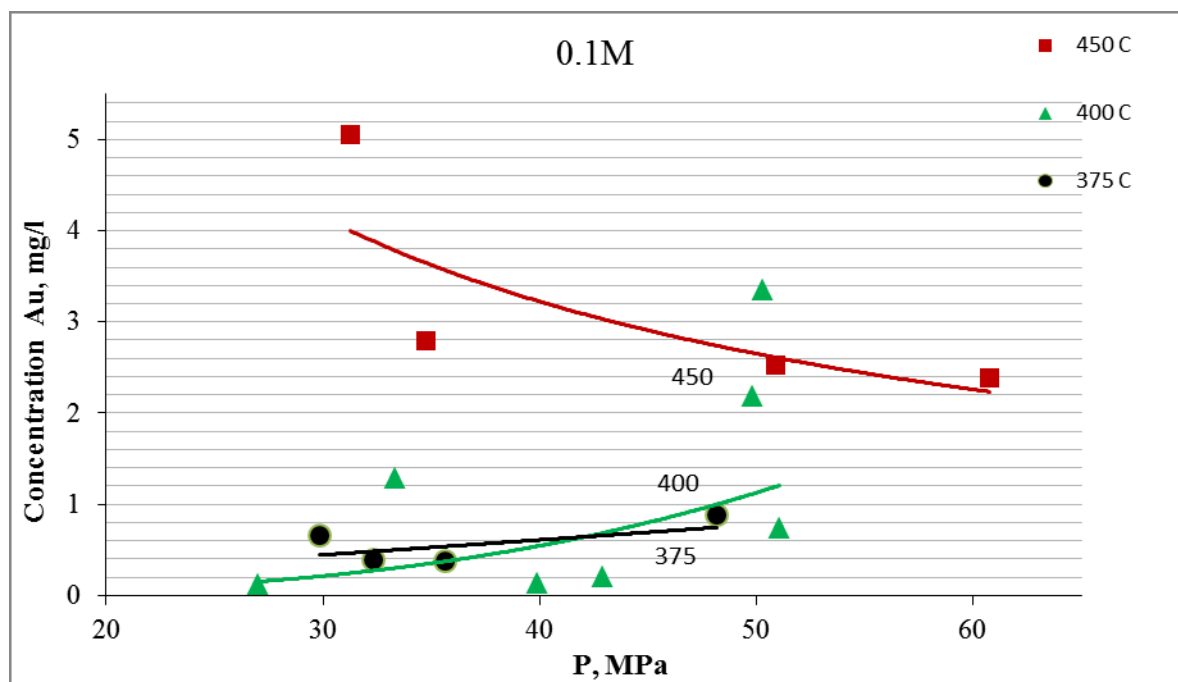


Fig. 3. Pressure dependence of Au content in the steam of 0.1M Na_2CO_3 solution in the temperature range 350÷500°C.

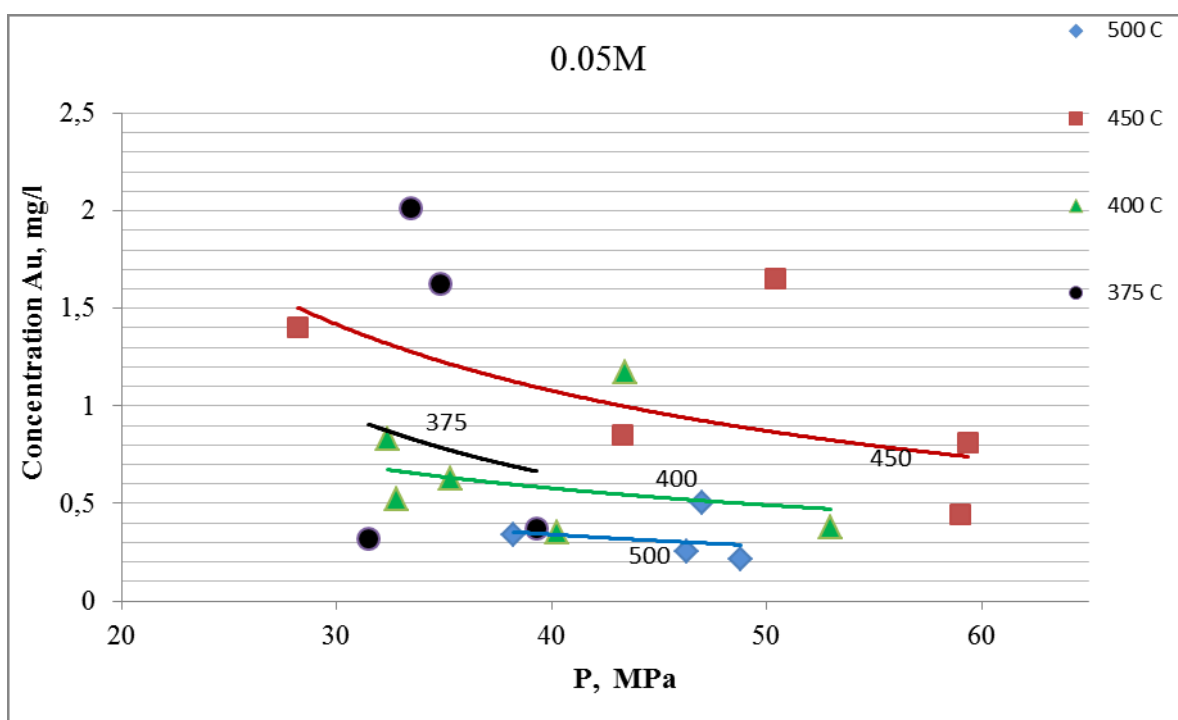


Fig. 4. Pressure dependence of Au content in the steam of 0.05M Na_2CO_3 solution in the temperature range 350÷500°C.

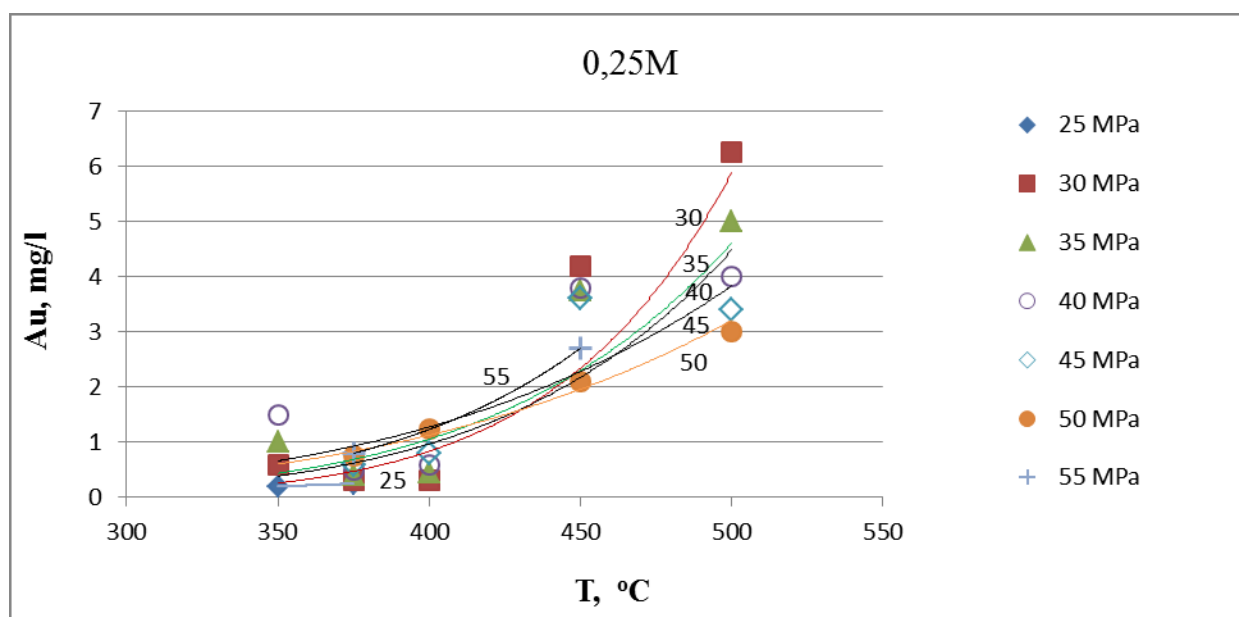


Fig. 5. Dependence of Au content in the steam of 0,25M Na_2CO_3 solution on temperature in the pressure range 25-55 MPa.

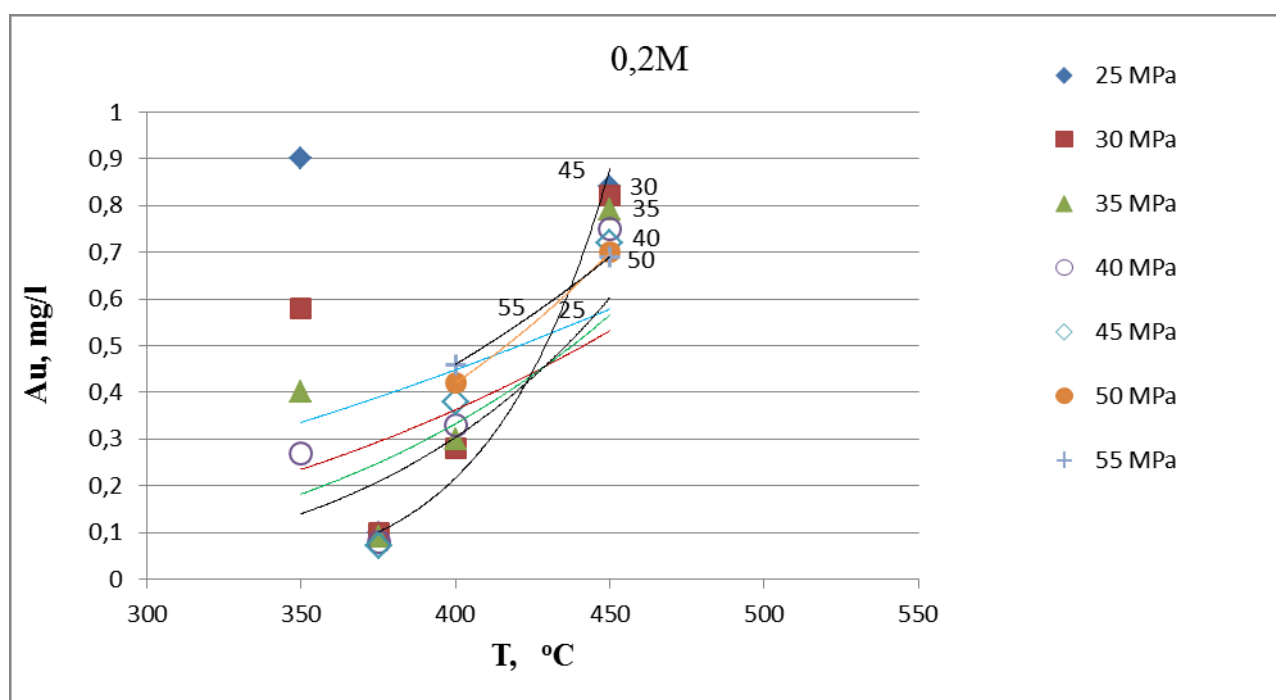


Fig. 6. Dependence of Au content in the steam of 0.2M Na_2CO_3 solution on temperature in the pressure range 25-55 MPa.

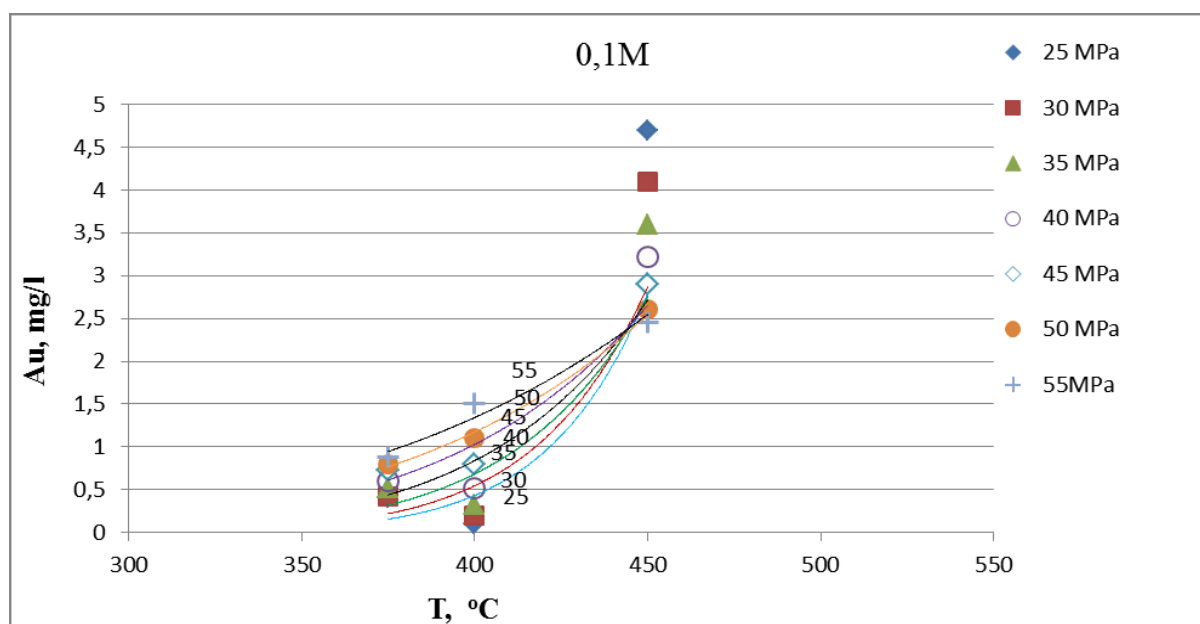


Fig. 7. Dependence of Au content in the steam of 0.1M Na_2CO_3 solution on temperature in the pressure range 25–55 MPa.

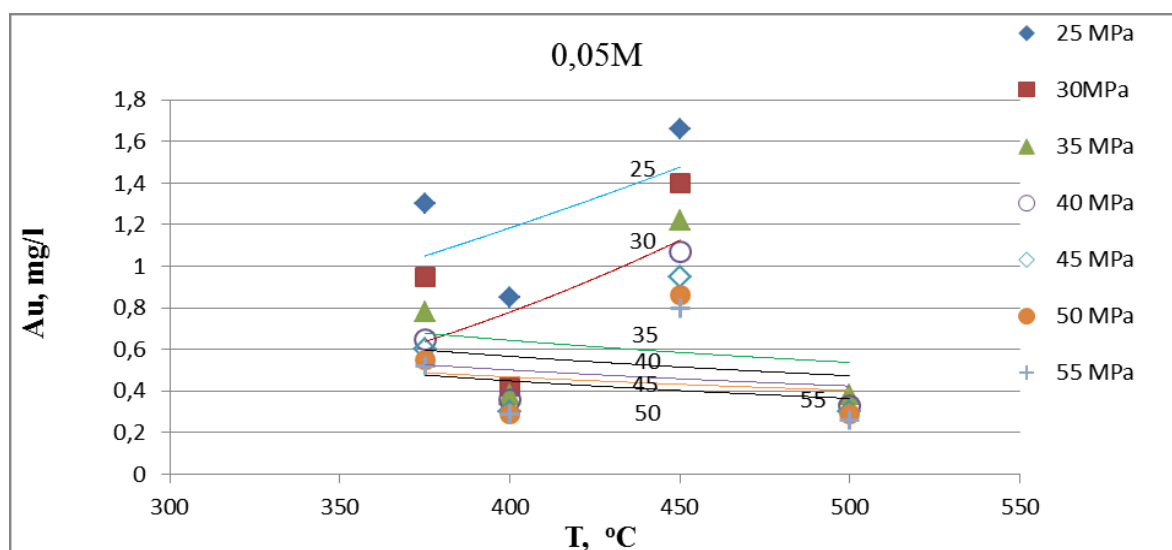


Fig. 8. Dependence of Au content in the steam of 0.05M Na_2CO_3 solution on temperature in the pressure range 25–55 MPa.

As it is seen in the drawing gold in 0.05M Na_2CO_3 solution behaves extraordinary – its concentration slightly decreases with temperature at pressure of 40–55 MPa, but grows with further temperature increase at pressure of 25–35 MPa as for Na_2CO_3 solutions having higher concentration.

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Kotova N.P. Experimental study of Nb_2O_5 solubility in chloride solutions at 300-550° C and 100 MPa

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Abstract. The dependence of Nb_2O_5 solubility as a function of chloride concentration was investigated in HCl, KCl, NaCl, and LiCl solutions with concentrations from 0.01 to 2 m at 550 °C and 100 MPa, as well as in solutions of LiCl at $T = 300^\circ\text{C}$ and $P = 100$ MPa under Co-CoO oxidizing conditions. The run duration was 30 days at $T = 300^\circ\text{C}$ and 18 days at $T = 550^\circ\text{C}$. It was found that Nb_2O_5 solubility is low with concentrations on the order of 10^{-4} to 10^{-5} m in the aqueous chloride solutions of different cationic composition (HCl, KCl, NaCl, and LiCl).

Key words: experiment, oxide niobium, hydrothermal solubility, chloride solutions.

Citation: Kotova N.P. (2015) Experimental study of Nb_2O_5 solubility in chloride solutions at 550 °C and 500 bar, *Experimental geochemistry*, V. 3. N

http://exp-geochem.ru/JPdf/2015/XX/XXXXXX_rus.pdf

Development of new criteria of prediction criteria and the search of rare metal deposits of Ta and Nb requires a clear understanding of the conditions of their formation. The urgency of the problem is the need to attract the experimental methods for

obtaining currently lacking quantitative estimates of possibility of hydrothermal transport and deposition of tantalum and niobium at the physico-chemical conditions typical for the formation of the main types of endogenous deposits of these metals associated with "apogranites" pegmatites, alkaline metasomatic rocks, alkaline syenites and carbonatites. As you know, there are various hypotheses of the genesis of these deposits - magmatic and hydrothermal-metasomatic. We attempted to look at the problem of the origin of these deposits, taking into account the results of experiments that can provide geologists some new criteria and limitations on the interpretation of geological data and to estimate the degree of hypothesis reliability [Kotova, 2014; Korzhinskaya et al., 2014].

The solubility of niobium oxide (Nb_2O_5) - analog of the natural mineral nioboksid as a function of the total chloride concentrations has been investigated. Experiments were carried out on high pressure hydrothermal apparatuses in sealed platinum capsules by double capsule method, allowing the use of solid-phase oxygen buffers, isolated from the capsules. The dependence of Nb_2O_5 solubility as a function of chloride concentration was studied in

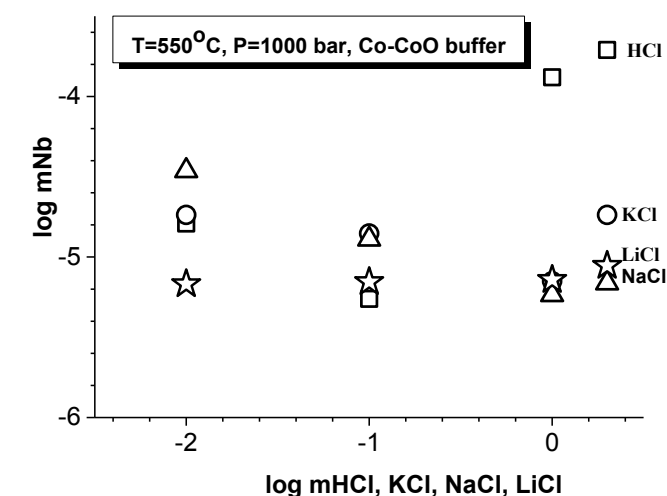


Fig. 1. Concentration dependence of Nb_2O_5 solubility in HCl, KCl, NaCl, and LiCl solutions at 550° C, 100 MPa and Co-CoO buffer conditions.

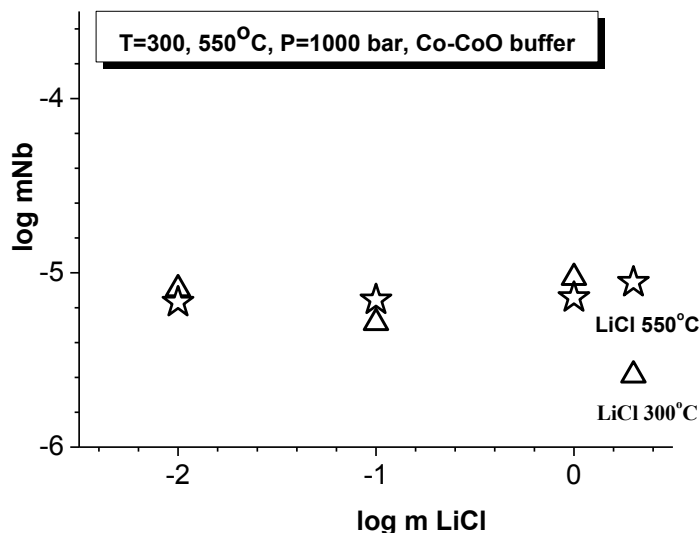


Fig. 2. Concentration dependence of Nb_2O_5 solubility in LiCl solutions at 300-550° C, 100 MPa and Co-CoO buffer conditions.

HCl, KCl, NaCl, and LiCl solutions with concentrations from 0.01 to 2 m at 550 °C and 100 MPa, as well as in solutions of LiCl at T = 300 °C and P = 100 MPa under Co-CoO oxidizing conditions. The run duration was 30 days at T = 300 °C and 18 days at T = 550 °C. To control congruent or incongruent dissolution of Nb oxide and to determine chemical composition of newly-formed phases (in case of their manifestation) the initial materials and solid run products were studied by X-ray diffraction, and electron microprobe analysis (Cam Scan MV 2300 (VEGA TS5130MM)).

The quenched aqueous solutions were analyzed by ICP/MS (Inductively Coupled Plasma Mass Spectrometry) and ICP/AES (Atomic Emission Spectroscopy) procedures for Nb, Ta, Mn, and Fe and admixture elements: Ti, W, Sn, K, and Na.

The experimental results are shown in Fig. 1 and 2. It appears that, at low concentrations of HCl with increasing HCl concentration, the niobium content in the solution decreases to $10^{-4.8}$ mol / kg H₂O in 0.01m HCl and to $10^{-5.3}$ mol / kg H₂O in 0.1 m HCl. At high HCl concentration (1m and higher) the niobium content increases, reaching a maximum value of $10^{-3.7}$ mol / kg H₂O in 2 m HCl.

The dependence of Nb₂O₅ solubility on KCl concentrations follows negative trend. With increasing concentration of potassium chloride, the niobium content in the solution decreases to $10^{-4.7}$ mol / kg H₂O in 0.01m KCl and to $10^{-5.2}$ mol / kg H₂O in 1 m KCl, and then slightly increases to a value of $10^{-4.7}$ mol / kg H₂O in 2 m KCl. Thus, can conclude that the solubility of Nb₂O₅ in KCl solutions at low concentrations is of the same order as in the HCl solution, and in the concentration range of 1 to 2 m it is an order of magnitude lower.

The dependence of Nb₂O₅ solubility on NaCl concentrations follows negative trend, by analogy with the solutions of KCl. With increasing concentration of sodium chloride, the niobium content in the solution decreases to $10^{-4.5}$ mol / kg H₂O in 0.01m NaCl and to $10^{-5.2}$ mol / kg H₂O in 1 m NaCl. In 2 m NaCl solution, the niobium content increases by only about 0.1, reaching a value of $10^{-5.1}$ mol / kg H₂O.

In solutions of LiCl with increasing concentration of chloride the niobium content practically does not change, remaining within $10^{-5.2}$ mol / kg H₂O.

According to our experimental data (Fig. 2) the decreasing temperature to 300 °C does not affect the solubility of niobium in LiCl solution. Decrease in the concentration of niobium to $10^{-5.2}$ mol / kg H₂O was observed only in 2 m LiCl solution.

The study of solid products by X-ray diffraction shows that over all investigated range of concentrations in chloride solutions niobium oxide dissolves congruently without changing the

composition. An exception is the data on the solubility of niobium oxide in 1 and 2 m LiCl solutions at T = 550 °C and P = 100MPa where Nb₂O₅ has incongruent solubility. Lithium niobate (LiNb₃O₈) is formed.

The great importance for understanding the genesis of hydrothermal Nb and Ta deposits has experimentally established fact of the low solubility of Nb₂O₅ in chloride solutions (HCl, NaCl, KCl and LiCl). The experimental data show that, for the range of conditions considered in this study, both at low and high concentrations of chlorides, the solubility of niobium is low and is within 10^{-5} - 10^{-4} m. This study demonstrates that chloride hydrothermal solutions are much less effective in transporting Ta and Nb. They are not capable of transferring these metals in the amounts sufficient for the formation of commercially viable ore deposits.

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Mironenko M.V. and Cherkasova E.V. Thermodynamic-kinetic modeling chemical weathering basaltic tephra of the island of Hawaii

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Abstract. A thermodynamic-kinetic model for interactions in water-rock systems has been modified to calculate chemical reactions in flow of solution. We used published data on composition of atmospheric precipitates at Hawaii and their abundance in Kaka Falls area, the island of Hawaii, a level of surface runoff, age and initial composition of basaltic tephra, mineralogical zoning of laterites, to adjust such a parameter of the model as a degree of exposition of the surface of primary mineral grains to aqueous solution. The goal was an approximate agreement of scales of calculated and observed mineral alteration during certain time.

Keywords: kinetics, chemical thermodynamics, geochemical modeling, chemical weathering.

Citation: Mironenko M.V., E.V.Cherkasova. 2015. Thermodynamic-kinetic modeling chemical weathering basaltic tephra of the island of Hawaii. *Experimental geochemistry*. V. 3. N. http://exp-geochem.ru/JPdf/2015/XX/XXXXXX_rus.pdf

Introduction. Chemical-thermodynamic modeling has significant restrictions to calculate water-rock interactions at moderate temperatures, because it does not take into account rates of chemical reactions among minerals and aqueous solutions. Earlier a thermodynamic-kinetic model was developed to describe a chemical evolution of water-rock systems in time [Mironenko & Zolotov, 2012; Zolotov & Mironenko, 2007]. It is based on a partial equilibrium principle and on assumption that secondary minerals form via a stage of dissolution of primary minerals, which is a limiting stage of the process [Helgeson, 1968]. Rates of mineral dissolution r_i are individual for different minerals and depend on temperature, pH, and a degree of solution saturation. Our experience showed that the model is able to calculate correctly consequence of mineral forming and evolution of chemical composition of aqueous solution, but it is not clear, how adequately it calculates a real duration of the process in time. Here, we attempt to adjust a model using data on approximate duration of weathering basaltic tephra, its initial chemical and mineral composition and porosity, size of mineral grains, chemical composition and abundance of rainfall. The goal was to reproduce numerically approximate real rate of weathering. Because parameters of equations of mineral dissolution rates are determined, as well as a flow of water and sizes of mineral grains are specified, the only parameter to adjust is a degree of exposition of primary mineral surface area to water solution. That parameter may be treated as a bulk structural property of the rock, which reflects a mineral contact with aqueous solution.

Short description of the model. Temperature dependence of a rate of chemical reaction r_T is described by Arrhenius equation:

$$r_T = r_{T_0} \cdot \exp \left[\frac{E_a}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right],$$

where r_{T_0} and r_T are rates at temperatures T_0 and T ; E_a is an apparent activation energy. The decrease in the rate of dissolution reaction as equilibrium is approached, according to transition state theory [Lasaga, 1981; Brantley, 2004], is simulated by the equation

$$r = r_T \left\{ 1 - \exp \left[p \left(\frac{\Delta G}{RT} \right)^q \right] \right\},$$

where ΔG is a driving force of reaction, which reflects a degree of saturation of solution with respect to a mineral. Coefficients p и q are adjustable parameters obtained by fitting near-equilibrium kinetic data available for some minerals.

Experimentally measured rates of congruent dissolution of the most of minerals can be presented as function of pH by empiric equation [Kump et al., 2000; Brantley, 2004]

$$r = k_H(a_{H^+})^n + k_{H_2O} + k_{OH}(a_{OH^-})^m,$$

where a_{H^+} и a_{OH^-} are activities of ions H^+ и OH^- ; k_H , k_{H_2O} , k_{OH} , n и m – fitting parameters for various minerals. Here we used kinetic parameters from [Brady & Walther, 1989; Brantley, 2004; Brantley et al., 2008; etc.].

Weathering is modeled as series of consecutive equilibrations in aqueous solution calculated at each time step k . For each equilibrium computation, mass balance b_{jk} for every chemical element j is calculated from the chemical composition of aqueous solution at the previous step $b_{j,k-1(aq)}$ and masses of minerals Δx_{ik} to be dissolved: $b_{jk} = b_{j,k-1(aq)} + \sum \Delta x_{ik} \nu_{ji}$, where ν_{ji} is a number of stoichiometric units of j th chemical element in a formula of a mineral i . $\Delta x_{ik} = S_{ik}^{ex} r_{ik} \Delta t_k$, where S_{ik}^{ex} is the exposed surface area of the i th mineral (m^2), proportional to geometric surface area via some coefficient: $S^{ex} = F s_i \cdot S_i^g$, Δt_k is duration of a time step (s), r_{ik} is a current rate of dissolution ($mole \cdot m^{-2} \cdot s^{-1}$). Minerals, deposited at previous time steps, are supposed as primary ones and can be dissolved if are not in equilibrium with solution. The duration of each time step was determined numerically from a specified molar amount of the fastest dissolving mineral. Therefore similar masses were introduced into solution during each time step to prevent significant change of pH. Geometric surface areas of minerals are calculated from their volumes in the rock and initial grain sizes, in further they change in time due to dissolution or deposition

Calculation of interactions in flow supposes that every out coming portion of solution replaces previous portion in underlying layer. That demands the constant short duration of time steps for all layers and results in significant increase of time of computation

Input data. Normalized mineral composition to fresh basaltic tephra of the Island of Hawaii [Hay & Jones, 1972 (Table 2, Column 1)] is as follow (mole per kg): Olivine (Fa0.5Fo0.5) 0.232; Clinopyroxene (Di0.5Hc0.5) 1.834; Orthopyroxene (Mg0.75Fe0.25) 1.162; Plagioclase (Oligoclase) 1.5; Ilmenite 0.32; Magnetite 0.103. A grain size for all minerals is 0.001 mm. Porosity of a tephra is 36%. The work [Hay & Jones, 1972] also describes chemical and mineral alteration during weathering, compositions and pH of pore waters of variously altered tephra. The age of basalts and thus a time of weathering does not exceed 10000 years.

Based on a paper [Parungo et al., 1982] on chemical composition of cloud water over Hawaii, we took a model salt composition of atmospheric precipitates (Na^+ $1 \cdot 10^{-4}$; Cl^- $2 \cdot 10^{-4}$; SO_4^{2-} $1 \cdot 10^{-5}$ mole/kg H_2O ; pH=5.68). Average rainfall in the area of Kaka Falls, according to [Hay & Jones, 1972] is accepted as 600 cm/year. Surface runoff aggregates 40%.

We took a 11-component system: O, H, Mg, Ca, Al, C, Si, Ti, Na, Cl, Fe; 35 potential minerals, 48 aqueous species. The system was open with respect to atmospheric oxygen and carbon dioxide. Temperature was taken as 298.15 K.

The proportions of rainfall and surface runoff, and basaltic tephra porosity and density suppose that at selected duration of a time step $\Delta t = 0.003$ year, water/rock ratio is equal to 0.12 for a rock column of 8.33 dm.

A degree of exposition of surface area to solution F_{s_i} for all primary minerals was taken as $1 \cdot 10^{-3}$, $1 \cdot 10^{-2}$ и $1 \cdot 10^{-1}$ for different series of calculations. For secondary minerals F_{s_i} was assumed much higher, as 0.4.

Results of calculations. Calculations for different values of F_{s_i} have shown that the most real rates of dissolution of primary minerals are obtained at $F_{s_i} = 10^{-2}$ (Fig. 1). During 10000 years of weathering at that value of F_{s_i} , olivine, plagioclase and clinopyroxene have been completely dissolved in the upper layer of a weathering zone, there are only remains of orthopyroxene. That is in agreement with petrographic descriptions [Hay & Jones, 1972]. The

results of calculation of passing of chemical weathering in consecutive layers of basaltic tephra in time for $F_s = 10^{-2}$ are shown in Fig. 2. We tried to find the most detailed and formalized description of the case study, that we used. The work [Hay & Jones, 1972] not completely meets these requirements but it is the best that we could find. Nevertheless, it is clear that the model adequately reproduces the main features of chemical weathering of basaltic tephra of the island of Hawaii, as formation in the upper layer red aluminum-ferric (gibbsite-goethite) laterite, accompanied by leaching of other chemical elements to underlying layers, where palagonites form. In [Hay & Jones, 1972]. "both palagonite and clay are used as physical, not mineralogical terms". Nevertheless, according to outward appearance palagonite corresponds to mineral assemblage "kaolinite + montmorillonites + zeolites". It should be noted, that montmorillonites and zeolites were formed in the model only at $F_s = 10^{-3}$, i.e. less washed primary minerals. The model also adequately describes a chemical balance of the profile of weathering (Fig. 3).

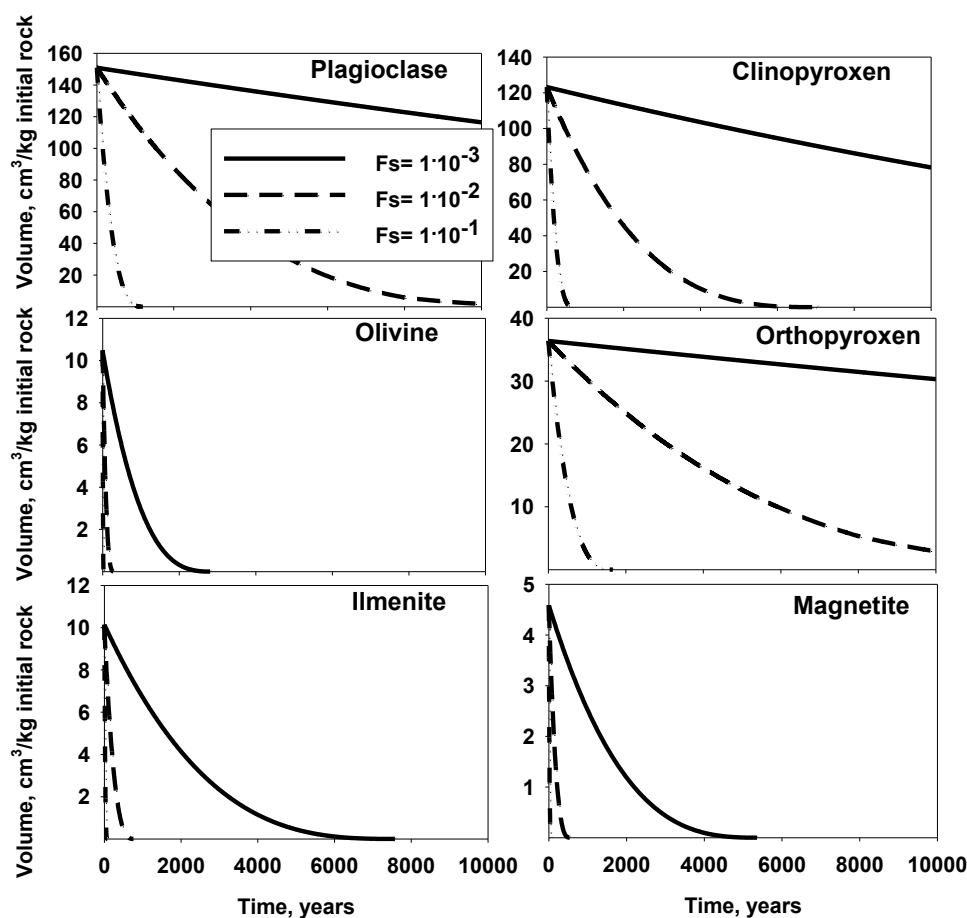


Fig. 1. Volumes of remaining primary minerals in the upper layer of the profile of residual soil in time for various values of the parameter F_s .

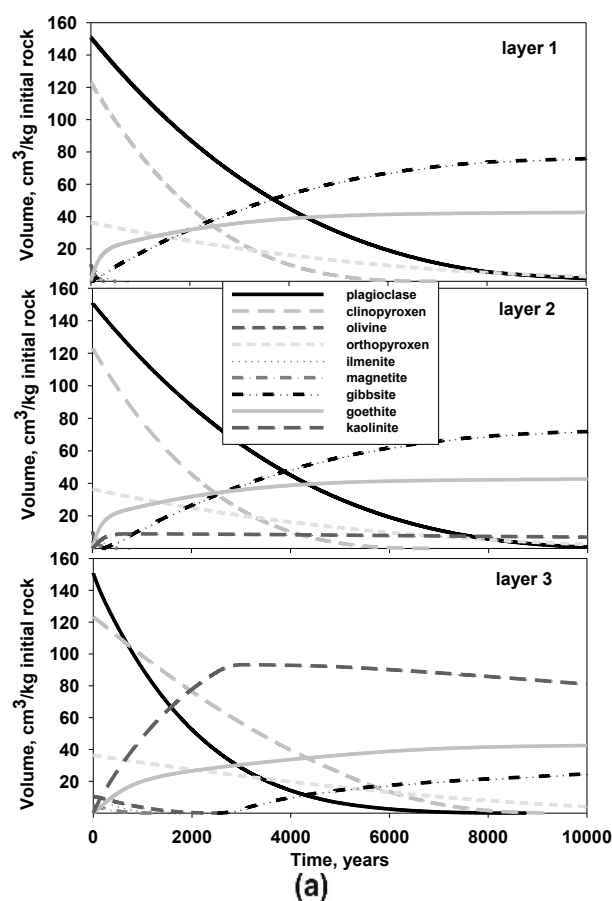


Fig. 2. Dissolution of primary minerals and formation of secondary minerals during chemical weathering basaltic tephra in three consecutive layers. $F_s = 10^{-2}$.

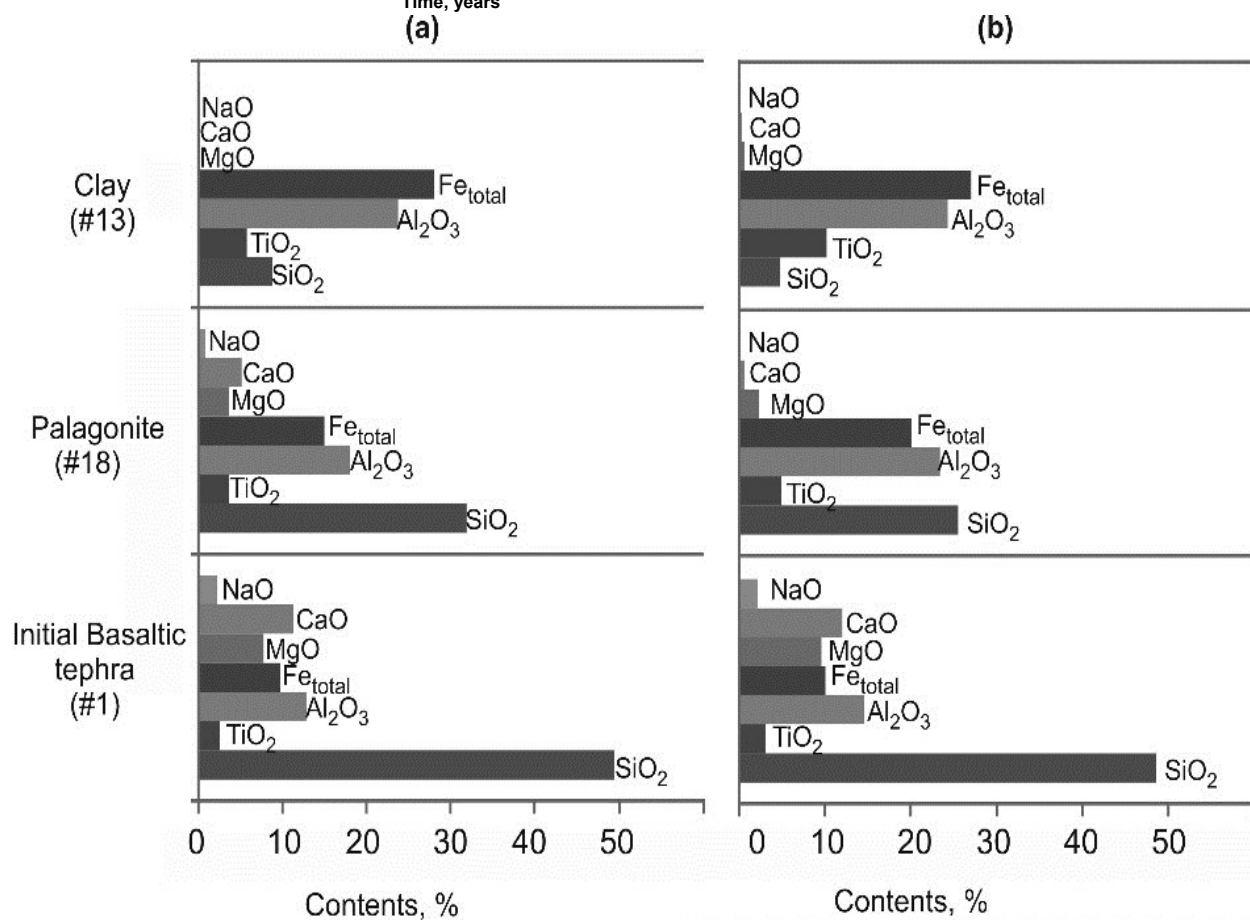


Fig. 3. Change of chemical composition of basaltic tephra of Kaka Falls area as a result of chemical weathering. (a) [Hay & Jones, 1972, Table 2], there are numbers of samples in parenthesis; (b) calculated in the model

Abstracts

In Table acidity and mineralization of pore solutions of differently weathered basaltic tephra from [Shvartsev et al., 2007] are shown in comparison with calculated values.

Degree of alteration of the rock	pH		Mineralization, g/l	
	[Shvartsev, 2007]	Calculated	[Shvartsev, 2007]	Calculated
Poorly altered basaltic tephra	7.6-7.8	7.75(40 years, Layer 2)	0.2-0.25	0.03 (40 years, L. 2)
Hardly altered basaltic tephra	≤6.0	5.84(10000 years, L. 3) 5.68 (10000 years, L.1)	≤0.1 g/l	0.007(10000 years, L.1)

Conclusions

1. Kinetic-thermodynamic model of formation of profile of weathering of basaltic tephra in time was developed. The model reproduces mineral and chemical zoning of the profile of altered basaltic tephra of Kaka aria of the island of Hawaii.

2. The model was adjusted with respect to accessibility of surface area of primary minerals to water flow so as calculated rock alteration after 10000 years of weathering to be similar to observed altered rock.

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