

PHYSICOCHEMICAL PROCESSES IN ICE AND PERMAFROST

NITROGEN COMPOUNDS IN CHEMICAL WEATHERING OF PERMAFROST:  
CONSTRAINTS FROM THERMODYNAMIC MODELING

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The role of nitrogen compounds in chemical weathering of permafrost has been studied by means of thermodynamic modeling. The experimental and modeling results show that oxides of nitrogen and sulfur present in air become involved in acid rains and cause a significant impact on chemical reactions in permafrost and increase the mobility of elements in weathering profiles at tailings sites. This impact should be taken into account when assessing the environmental effects of mining, which is illustrated by the case of a copper field in Northern Transbaikalia.

*Cryogenesis, nitrogen compounds, chemical weathering, sulfide tailings, environment, thermodynamic modeling*

INTRODUCTION

Northern Transbaikalia stores abundant noble, radioactive, rare, and base metals, and most of geoscience research in the region focuses on issues of metallogeny and mineral exploration [Blinov *et al.*, 2014]. The rich mineral deposits are however difficult to develop because of transportation and infrastructure problems, as well as harsh climate and permafrost, terrain ruggedness, and high seismicity. The exploration and mining thus require large investment while the market conditions are not very favorable. Some commercial interest to the territory has rekindled due to renovation of the Baikal-Amur railway [Falyakhov, 2013], and some increase in industrial activity is expected for the nearest future. In this respect, it is important that the environment impacts of mining and storage of wastes and the ways of prevention and remediation of their contamination effects were predicted and taken into consideration since the feasibility assessment of development projects.

The environment impacts from exploration and mining are quite strong in the area of the Kodar and Udokan ranges separated by the Chara basin. Mining and ore processing wastes in the area are often stored improperly being exposed to chemical weathering and thus pose high pollution risks. Increasing emission of sulfur and nitrogen and related acid rains are additional aggressive leaching agents that act upon minerals in tailings [Chanturiya *et al.*, 1999]. Recent experimental data show that nitrogen oxides and products of their reaction with water (e.g., HNO<sub>2</sub>) in acid rains accelerate acid leaching of sulfide minerals

[Markovich and Ptitsyn, 1998], and this effect is especially prominent in zones of negative temperatures [Pavlyukova and Markovich, 2006]. Cryogenic and geochemical processes involving nitrogen compounds in supergene environments remain poorly understood, and their role in acceleration of dissolution has been neglected so far. Meanwhile, publications are appearing on the inputs and migration of nitrogen compounds induced by mining in permafrost terrains [Makarov, 2012]. These compounds may influence significantly the natural chemical weathering patterns in shallow permafrost and maintain conditions for active acid leaching of sulfide wastes.

STUDY AREA

We study the impact of nitrogen compounds on chemical weathering of permafrost in the area of the Russia's largest and the world's third largest copper field of Udokan. It lies in the zone of almost continuous permafrost varying in thickness from 65 m under rivers to 950 m under watersheds. The temperature of frozen ground is  $-7$  to  $-8$  °C, the active layer is about 1 m thick, and the depth of zero annual amplitudes reaches 20–30 m [Kuzmin and Polyakov, 2003].

The Udokan ores and ore-bearing rocks store more than 100 mineral species: sulfide primary ores, abundant bornite Cu<sub>5</sub>FeS<sub>4</sub> and chalcocite Cu<sub>2</sub>S, less abundant chalcopyrite CuFeS<sub>2</sub>, sulfates and carbonates as secondary copper minerals produced by supergene alteration, and particular cryogenic minerals (hydroantlerite Cu<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>8</sub>·6H<sub>2</sub>O, hydrobro-

shantite  $\text{Cu}_5(\text{SO}_4)_4(\text{OH})_2 \cdot 5.24\text{H}_2\text{O}$ , udokanite  $\text{Cu}_8(\text{SO}_4)_3(\text{OH})_{10} \cdot \text{H}_2\text{O}$ , firboferrite  $\text{Fe}^{3+}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$  and other hydrated phases) [Kuzmin and Polyakov, 2003].

Check drilling in the Udokan copper field began in 2010, and exploratory sampling increased, in order to estimate the mineral resources according to the international classification of the Joint Ore Reserves Committee (JORC) Code. The field is supposed to be developed by conventional open-pit mining, with drilling and blasting operations [Environmental and Social Aspects..., 2010]. The mining-metallurgical integrated works, designed to be built in 2020, will produce annually 474,000 tons of copper and 277 tons of silver, with additional heap leaching of cut-off grade ore [Government..., 2014]. Note that the construction sites for industrial and social infrastructure will be located in intermontane valleys where the environment risks of contamination dispersion are especially high. Although the area lacks large industrial enterprises or other pollution sources yet, air monitoring at Novaya Chara village shows increasing concentrations of nitrogen dioxide and dust and, as a consequence, an extremely high potential for pollution [Environment..., 2008]. Further industrial development of the territory will pose still greater risks of air pollution with nitrogen compounds [Nedeshev et al., 2001].

## METHODS AND RESULTS

Physicochemical simulation is a good tool to gain insights into geochemical processes in permafrost. It can furnish new knowledge and provide thermodynamical interpretation of the existing data. The application of such simulation to permafrost geochemical systems is problematic, but new methods of thermodynamic calculations and correlations are appearing which allow for the heterogeneity of systems comprising multiple components in different phase states and for chemical changes at low temperatures [Gurevich et al., 2001; Mercury et al., 2001; Bychinsky et al., 2008]. We have simulated chemical weathering

with participation of nitrogen compounds in a model system ‘water–rock–gas’ in order to assess the impact of N-bearing acid rains on oxidation of sulfides and secondary mineralization in the real conditions of the Udokan field. The phase relations in the system ‘water–rock–gas’ were calculated using the *Selektor* software based on Gibbs energy minimization [Chudnenko, 2010]. The thermodynamic system was assumed to be open with respect to the atmosphere. The compositions of equilibrium phases were found at positive (+20 °C) and negative temperatures (–20 °C) and a pressure of 1 bar.

The multiphase and multicomponent model system consisted of 12 independent elements: C–Cu–S–Fe–Si–Al–Ca–Ti–N–Zr–H–O. Phase equilibrium in this system was possible for 105 dissolved compounds, 9 gases, and 266 solids, altogether 380 probable related components.

We used the a\_sprons98.DB, g\_sprons98.DB [Johnson et al., 1992] and s\_Yokokawa.DB [Yokokawa, 1988] thermodynamic databases for liquid, gas, and solid phases, respectively. Ice was considered as another solid, with its thermodynamic properties borrowed from [Mercury et al., 2001]. In addition, the model included the Gibbs free energy ( $\Delta_f G$ ) of some hydrates that may exist in supergene environments (Table 1), with their formation enthalpy ( $\Delta_f H^\circ$ ) and entropy ( $S^\circ$ ) in the standard state (298.15 K; 1 bar) according to [Ryabin et al., 1977; Mercury et al., 2001].

Acid leaching of sulfides was simulated in the model system assuming interaction of 1 kg  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$  of different concentrations (0.5; 0.05; 0.005 and 0.0005 mol), a solid (sulfide ore) and 100 kg of air (Table 2). The range of  $\text{H}_2\text{SO}_4$  concentrations from 0.5 to 0.0005 mol was chosen proceeding from its large range (pH 1–0.46  $\text{H}_2\text{SO}_4$ ) in naturally occurring weathering profiles of sulfide deposits [Nordstrom, 1991]. The existence of such aggressive waters is still more probable in permafrost due to cryogenic concentration.

Table 1. Thermodynamic properties of ice, hydrates, and nitrogen

Solid phase	Formula	Entropy, cal/mol	Gibbs free energy, cal/mol	Enthalpy, cal/mol
Poitevinite	$\text{CuSO}_4 \cdot \text{H}_2\text{O}$	34.895	–219 460	–259 520
Bonattite	$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$	52.892	–334 649	–402 560
Chalcanthite	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	71.797	–449 344	–544 849
Copper nitrate	$\text{Cu}(\text{NO}_3)_2$	–72 978.01*	–20 895.5**	26.051*
Copper nitrate trihydrate	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	–291 085.086*	–200 017**	62.5**
Copper nitrate hexahydrate	$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	–504 326.003*	–374 259*	98.9*
Copper nitrate nanohydrate	$\text{Cu}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$	–720 810.946**	–551 807**	135.51**
Ice	$\text{H}_2\text{O}$	10.700	–56 546	–69 968

\* Values borrowed from [Ryabin, 1977].

\*\* Tentative values inferred from additivity of ice-like water in hydrates [Mercury et al., 2001].

Table 2. Mineral chemistry and contents of sulfide ore used for thermodynamic modeling with *Selektor* software

Minerals	Formula	Contents in samples, %	Molecular mass	Molal content
Anortite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	38.84	278.207	0.139 608
Bornite	Cu <sub>5</sub> FeS <sub>4</sub>	0.10	501.841	0.000 199
Brochantite	Cu <sub>4</sub> (SO <sub>4</sub> )(OH) <sub>6</sub>	0.06	452.292	0.000 133
Ilmenite	FeTiO <sub>3</sub>	0.04	151.225	0.000 265
Quartz	SiO <sub>2</sub>	40.0	60.084	0.665 735
Limonite	FeOOH·(Fe <sub>2</sub> O <sub>3</sub> ·nH <sub>2</sub> O)	0.43	88.854	0.004 839
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	6.60	231.539	0.028 505
Chalcocite	Cu <sub>2</sub> S	13.87	159.158	0.087 146
Chalcopyrite	CuFeS <sub>2</sub>	0.02	183.525	0.000 218
Zircon	ZrSiO <sub>4</sub>	0.10	147.395	0.000 680

 Table 3. Model composition of rain water with NO<sub>2</sub> impurity

Phase	Related components
Rain water	H <sub>2</sub> O, NO <sub>3</sub> <sup>-</sup> , N <sub>3</sub> <sup>-</sup> , N <sub>2</sub> <sup>-</sup> , NH <sub>3</sub> <sup>0</sup> , NH <sub>4</sub> <sup>+</sup> , NH <sub>4</sub> N <sub>3</sub> <sup>0</sup> , HNO <sub>2</sub> <sup>0</sup> , NH <sub>4</sub> NO <sub>3</sub> <sup>0</sup> , NH <sub>4</sub> OH <sup>0</sup> , NH <sub>4</sub> NO <sub>2</sub> <sup>0</sup> , HNO <sub>3</sub> , H <sub>2</sub> CO <sub>3</sub> <sup>0</sup> , HCO <sub>3</sub> <sup>0</sup> , HCO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , CH <sub>4</sub> <sup>0</sup> , O <sub>2</sub> <sup>0</sup> , H <sub>2</sub> <sup>0</sup> , N <sub>2</sub> <sup>0</sup> , Ar <sup>0</sup> , He <sup>0</sup> , Kr <sup>0</sup> , Ne <sup>0</sup> , OH <sup>-</sup> , H <sup>+</sup>
Air	N <sub>2</sub> , NO <sub>2</sub> , NH <sub>3</sub> , CO, CO <sub>2</sub> , CH <sub>4</sub> , O <sub>2</sub> , H <sub>2</sub> , Ar, He, Kr, Ne

In order to take into account the presence of 0.085 mg/m<sup>3</sup>NO<sub>2</sub> (2.9 times the maximum admissible concentration) in the air of the study area [*Environment...*, 2008], 0.005 358 mol of nitrogen dioxide were added to the model gas phase prior to the calculations.

The physicochemical interactions in the model system ‘water–rock–gas’, with NO<sub>2</sub> added to the gas phase per 100 kg air, lead to the formation of rain water having a pH lower than in the natural non-contaminated atmospheric moisture with CO<sub>2</sub> but without impurities (4.5 against 5.6). As the modeling predicts, the liquid phase of the system (rain water) may contain diverse nitrogen components (Table 3): NO<sub>3</sub><sup>-</sup>, N<sub>3</sub><sup>-</sup>, N<sub>2</sub><sup>-</sup>, NH<sub>3</sub><sup>0</sup>, NH<sub>4</sub><sup>+</sup>, NH<sub>4</sub>N<sub>3</sub><sup>0</sup>, HNO<sub>2</sub><sup>0</sup>, NH<sub>4</sub>NO<sub>3</sub><sup>0</sup>, NH<sub>4</sub>OH<sup>0</sup>, NH<sub>4</sub>NO<sub>2</sub><sup>0</sup>, and HNO<sub>3</sub>. Therefore, there is high probability of acid rains during drilling and blasting in the Udokan field, given that high (NO<sub>2</sub>) concentrations are already present in the air.

The local geography of the Chara basin, with its valleys and ranges, strongly continental climate, and temperature inversions, is favorable for acid precipitation and its involvement into acid leaching of metals. This inference has been proven experimentally [*Ptitsyn et al.*, 2009] and should be taken into account in predictions for amounts of acid moisture and environment impacts, especially at the sites of tailings.

The modeling places constraints on the formation conditions and compositions of secondary phases. The aqueous agents of acid leaching of sulfide ores at -20 °C and 20 °C (Fig. 1, a, curves 1 and 2, respectively) have mostly subalkaline pH ranges. The predicted values agree with the 5.67–7.64 range observed in the field [*Kuzmin and Polyakov*, 2003] for

supra-permafrost and surface waters, as well as for contamination trains of mine waters, which are due to their high carbonate contents and preferable leaching of oxidized ores. Sporadic zones of low pH (2.21, 2.62) occur in places where acid waters originally existed in high concentrations (e.g., in weathering profiles of sulfide ores) and sulfides became more strongly oxidized than minerals in the host rocks, while some gases became dissolved in ice. Weathering of sulfides exposed to open air notably increases Eh in acid waters (Fig. 1, b), but Eh values are roughly similar at positive and negative temperatures (compare curves 1 and 2 in Fig. 1, b).

The secondary phases that can precipitate in the supergene environment of the Udokan field at positive temperatures in open air (Table 4) include hydrates of copper sulfides: poitevinite CuSO<sub>4</sub>·H<sub>2</sub>O, bonattite CuSO<sub>4</sub>·3H<sub>2</sub>O and chalcantite CuSO<sub>4</sub>·5H<sub>2</sub>O. The equilibrium solids are quartz (SiO<sub>2</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>), aragonite (CaCO<sub>3</sub>), malachite (Cu<sub>2</sub>[(OH)<sub>2</sub>·CO<sub>3</sub>]), zirconium oxide (ZrO<sub>2</sub>) and rutile (TiO<sub>2</sub>). The precipitates (secondary minerals) differ only in amounts, which vary according to their chemical weathering conditions.

The solids that crystallize at low temperatures (to -20 °C) include ice and such minerals as halotrychite Fe<sup>2+</sup>Al<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>·22H<sub>2</sub>O, bilinite Fe<sup>2+</sup>Fe<sub>2</sub><sup>3+</sup>(SO<sub>4</sub>)<sub>2</sub>·22H<sub>2</sub>O, and rostitite Al[SO<sub>4</sub>](OH)·5H<sub>2</sub>O. The diversity of Cu, Fe and Al aqueous species is restricted to the domain of very low pH (0.5). Calcium sulfates (anhydrite CaSO<sub>4</sub>, bassanite CaSO<sub>4</sub>·0.5H<sub>2</sub>O and gypsum SO<sub>4</sub>·2H<sub>2</sub>O) are stable at both positive and negative temperatures.

The thermodynamic modeling, with atmospheric nitrogen and NO<sub>2</sub>, predicts (Table 4) precipitation of

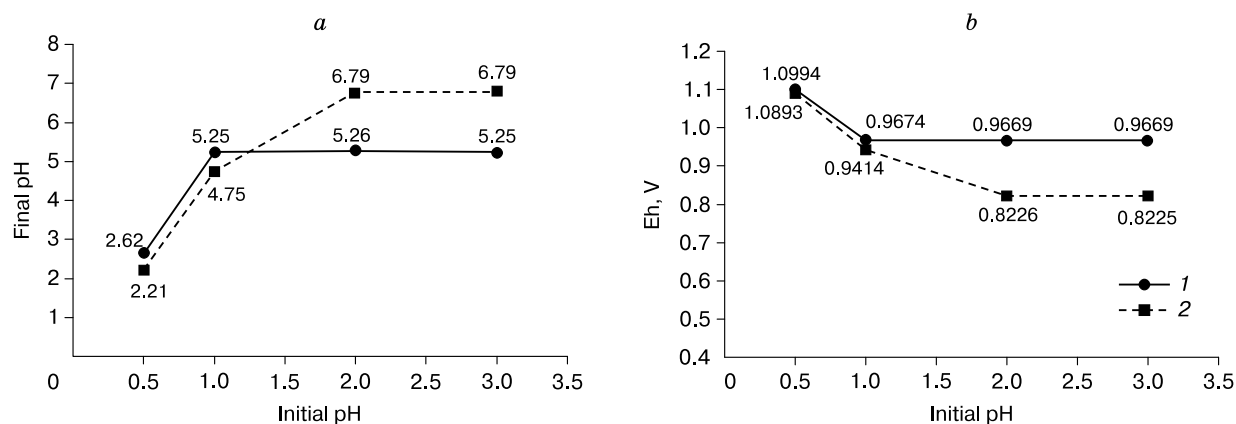


Fig. 1. pH (a) and Eh (b) ranges of aqueous species involved in acid leaching of sulfide ores at  $-20\text{ }^{\circ}\text{C}$  (curve 1) and  $20\text{ }^{\circ}\text{C}$  (curve 2).

Table 4. Predicted composition of solid secondary phases produced by acid leaching of sulfides with nitrogen compounds at different temperatures

Initial pH of waters	Mineral assemblage	
	$T = +20\text{ }^{\circ}\text{C}$	$T = -20\text{ }^{\circ}\text{C}$
0.5	Poitevinite ( $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ), bonattite ( $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ ), chalcantite ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), anhydrite ( $\text{CaSO}_4$ ), bassanite ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), chlorite ( $\text{FeAl}_2\text{SiO}_5(\text{OH})_2$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), zirconium oxide ( $\text{ZrO}_2$ ), quartz ( $\text{SiO}_2$ ), rutile ( $\text{TiO}_2$ )	Ice, bonattite, chalcantite, bilinite ( $\text{Fe}^{2+}\text{Fe}_2^{3+}(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ), halotrychite ( $\text{Fe}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ ), anhydrite, bassanite, gypsum, rostitite ( $\text{Al}[\text{SO}_4](\text{OH}) \cdot 5\text{H}_2\text{O}$ ), chlorites, hematite, zirconium oxide, quartz
1	Bonattite, chalcantite, anhydrite, bassanite, gypsum, antlerite ( $\text{Cu}_3[(\text{OH})_4/\text{SO}_4]$ ), hematite, zirconium oxide, quartz, rutile, chlorites	Ice, anhydrite, bassanite, gypsum, antlerite, chlorites, hematite, zirconium oxide, quartz
2	Anhydrite, bassanite, gypsum, chlorites, hematite, zirconium oxide, quartz, rutile, aragonite ( $\text{CaCO}_3$ ), malachite ( $\text{Cu}_2[(\text{OH})_2\text{CO}_3]$ ), calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ), copper nitrate hexahydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ )	Ice, anhydrite, bassanite, gypsum, antlerite, chlorites, hematite, malachite, zirconium oxide, quartz, rutile, calcium nitrate, copper nitrate hexahydrate
3		

copper and calcium nitrates ( $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ca}(\text{NO}_3)_2$ , respectively) in the domain of originally low pH (2–3). The formation of these phases is quite possible in the temperature range 0 to  $-20\text{ }^{\circ}\text{C}$  and is consistent with the  $\text{Cu}(\text{NO}_3)_2\text{-H}_2\text{O}$  phase diagram reported by Kirgintsev *et al.* [1972].

According to the modeling results, all physicochemical changes in the waters are in line with dissolution and leaching of primary phases and precipitation of secondary phases.

## CONCLUSIONS

1. Thermodynamic modeling can predict the compositions of the most probable solid, liquid, and gas equilibrium phases produced by acid leaching of sulfide ores in permafrost in the presence of nitrogen compounds. The parageneses of secondary minerals generally correspond to the assemblages found in the weathering profiles of the Udokan field.

2. Laboratory experiments [Paolyukova and Markovich, 2006] and thermodynamic modeling indicate that nitrogen compounds affect the patterns of chemical weathering in permafrost, especially at sites of waste dumps and tailings, which causes pollution of natural waters with heavy metals (specifically with copper). The presence of nitrogen compounds ( $\text{HNO}_2$ ) increases copper recovery from sulfide ore by a factor of 10 to 30.

3. The reported results can be further used to reconstruct geochemical processes and compile the respective actual and prediction maps. This mapping is based on available data of weather monitoring, chemical analyses of tailings and their mass balance calculations, as well as on digital elevation models to allow for terrain ruggedness [Demina *et al.*, 2013].

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