Migration of copper ions from an underlying substrate to the snowcover

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ABSTRACT: Migration of copper ions from an underlying substrate to the contact layer of the snowcover was studied. The concentration of copper ions, as well as the concentration of ions of the background electrolyte (NaCl) used in preparation of artificial frozen substrate blocks were found to correlate with the liquid-like phase content in a given temperature range. The ionic migration occurs at temperatures -12° C and higher. The difference in solvation between the migrating ions and the specific structure of the liquid-like film are the main causes for the differences in their migration properties.

1 INTRODUCTION

An understanding of the laws governing the movement of heavy metal compounds in a frozen system as a specific medium is important today in terms of both ecology and geochemistry. Heavy metal compounds are indicators of mineral deposits, as well as anthropogenic sources of elements. Therefore knowledge of the distribution of soluble substances, including copper compounds, in a frozen system is a prerequisite for proper interpretation of the geochemical information.

Frozen ground is a multicomponent, heterogeneous substrate, and being so, dictates the complexity of physico-chemical processes occurring in it. The major specific of these processes is that water exists in three phases: liquid, solid and gaseous. The liquid phase is the medium for solute migration. One of the components of liquid water is an unfrozen water film on the surface of mineral soil particles. A significant contribution to the migration process is made by a liquid-like film on the developed surface of fine-crystalline ice inclusions, which are in contact both with the soil particles and the pore air. Both films, which have structural differences, can contain solutes. When the solute concentration exceeds a certain limit a bulk solution phase may form, as is sometimes the case in nature.

Solutes can migrate in the unfrozen films in frozen ground under the influence of various factors. The migration ability of substances depends on their own physico-chemical properties and the properties of mineral and organic soil particles. Adsorption of dissolved components of the liquid phase on the surfaces of frozen soil solids (Fedoseyeva 2000) in the process of migration has a significant influence on the nature of distribution of substances in a heterogeneous medium.

Our earlier studies of copper ion adsorption on aluminium oxides simulating the surface properties of the main soil components, oxides and clays (Fedoseyeva & Bereznyaya 2001), demonstrated that the adsorption mechanism plays an important role in the movement of trace elements at low concentrations in a heterogeneous medium. The migration ability of copper species interacting with the surface hydroxyl groups of oxides and clays should be relatively greater at lower temperatures, because their concentration in the liquid phase increases due to a reduction in the adsorption affinity. The reason is reduced reactivity of the active surface groups due to a decrease in the ionic product of water (Tewari & Campbell 1976).

Thus the effect of the surface of mineral particles in frozen soils on the degree of movement of soluble species is evident. The results of our investigations on adsorption in river sand and on migration of gold compounds in a frozen substrate add considerable support for what has been stated above (Fedoseyeva & Streltsova 1993, Fedoseyeva 1998). However, little is presently known about the chemical migration effects of the surface of fine-crystalline (disperse) ice which is a typical constituent of frozen systems.

2 DISSOLVING PROPERTIES OF LIQUID-LIKE FILM ON ICE SURFACE

We carried out a series of investigations on the physico-chemical properties of the disperse ice surface (Fedoseyeva & Nechaev 1984). The study was made on snow crystals collected in the vicinity of Yakutsk after the first heavy snowfall on the leeward side. The sorptive properties of disperse ice for the organic substances dissolved in a solvent indifferent to the solid water phase were investigated in the temperature range of 0 to -25° C. We found that the sorptive properties of the ice were caused by the transfer of solute molecules into the liquid-like film, suggesting the dissolving action of the liquid-like phase. The greatest degree of sorption by the disperse ice is shown by the compounds with a high distribution coefficient between water and organic solvent. When the solute concentration in the system exceeded a critical limit, a bulk phase of aqueous solution was formed.

The experiments on sorption (Fedoseyeva & Nechaev 1984) demonstrated that a liquid-like film disappeared, if the disperse ice samples had been exposed for a long period (over two months) at temperatures below -40° C. At higher temperatures, a liquid-like film redeveloped no earlier than in 48 hours at -10° C, 15 hours at -5° C and 2.5 hours at -2° C. This suggests that the thickness of the liquid-like film on the surface of snow crystals, which has formed at higher temperatures or due to other effects, decreases to the lowtemperature equilibrium value over a long period of time. Therefore, the film thickness in the natural systems may be often greater than the equilibrium value due to variations in the temperature and moisture regimes. The large inertia of the liquid-like phase may be responsible for hysteresis in the temperature dependence of unfrozen water content in fine-grained soils such that "the amount of unfrozen water is larger in the freeze cycle than in the thaw cycle" (cited in Melnikov & Tolstikhin 1974).

3 METHODS OF RESEARCH

The ability of disperse ice to sorb the soluble compounds of gold from aqueous solutions at subzero temperatures (in the presence of a background electrolyte) was observed in Fedoseyeva & Fedoseyev (1989), suggesting the activity of the disperse ice surface in water systems. It is reasonable to infer that, if a frozen substrate and snow are in contact, the liquidlike film of snow crystals will act as a migration medium for movement of the solutes from unfrozen pore solutions in the soil substrate to the base of the snow in accordance with the general laws of concentration diffusion (Fedoseveva 2000).

The well-known fact that the first snow meltwater fractions are normally enriched in chemical substances (Supatashvili 1981) proves the presence of solutes in the surface layer of snow grains. The conditions and dynamics of migration of salt components from the underlying frozen soil to the base of the snow were investigated during long-term snowcover studies at a Central-Yakutian site (Fedoseyeva et al. 1986). The surface of the experimental site was cleared of vegetation before the establishment of a permanent snowcover in order to ensure the contact between the frozen substrate and the snow and to exclude contamination of the snow samples obtained from the base of the snow.

Regular measurements throughout the cold season included snow temperature (with thermistors), vapour transfer rates, specific surface area estimation (Fedoseyeva et al. 1980) of snow crystals, and solute concentrations. Measurements were made at intervals of 5-15 cm. It was found that solutes from the soil

substrate were transferred mainly to the lowest 5-10 cm layer of snow. Two maxima, the so-called "autumn" and "spring", were observed in the solute concentration dynamics. We inferred from the observation data that their appearance was determined by a variety of factors, but the sole cause was an increase in the liquidlike phase content and thus the migration of solutes from the liquid phase in the frozen substrate to the base of the snow in the liquid-like film. The "spring" maximum (under the conditions of moderate heating of the snow mass) was also confirmed by the experiments conducted on artificially prepared frozen blocks which contained soluble species of gold (Fedoseyeva & Fedoseyev 1991). The frozen blocks were placed at the base of the snowcover before the period of time favourable for upward migration of solutes toward the snowcover. The period for solute accumulation in the contact layer of snow was determined from our earlier long-term studies. It could have been extended provided there were conditions for more uniform daily temperature changes in the snow layer and thus for delayed melting.

In the 1994/95 season, experiments were set up to study the dynamics of the flux of copper ions into the contact layer of snow, because copper is a typical indicator of metal-containing mineral deposits. The experimental site was protected from the south with a fence painted white to reflect sunlight. The snow surface was shielded with a white cloth at a height of about 30 cm. Artificially frozen blocks, $60 \times 40 \times 5$ cm in size, containing polystyrene grains as a fill material were prepared and placed at the snowcover base. Electrolyte-containing solutions, 10^{-1} mole/l NaCl, 10^{-2} mole/l KCl and 10^{-2} mole/l CuCl₂, were used to prepare the blocks. When a solution is subject to freezing, solutes are concentrated by more than one order of magnitude. The initial pH value of 2.0 was selected so that only ions would be the migrating chemical forms of copper. The blocks amounted to monolithic ice cement, thus excluding contamination of snow samples. They were installed in the end of March. Temperature was measured with thermistors at the block surface - snow contact and at 5 cm above the contact surface. Snow samples were collected from the 5-cm thick contact layer at regular time intervals. After melting they were analysed for Cu²⁺, Na⁺, Cl⁻ contents. Copper was determined semi-quantitatively by the spectrographic technique, sodium by flame photometry, and chlorine ions by mercurometry.

4 RESULTS AND DISCUSSION

Observations of the concentration dynamics of added components and analysis of the data on temperature and the liquid-like film thickness – temperature relationship



Figure 1. Changes in the logarithm of equilibrium thickness (d, nm) of the liquid-like film (calculated according to Kvlividze et al. 1974) on the snow crystal surfaces and in the logarithm of concentration (C, mole/l) of copper (Cu²⁺), sodium (Na⁺) and chloride (Cl⁻) ions in the contact layer of snow during the observation period, spring 1995.

(in the state of equilibrium) (Kvlividze et al. 1974) revealed clear correlation between the liquid-like phase content and the solute concentrations (Fig. 1). The observed correlation confirms the importance of the liquid-like film on disperse ice surface in the chemical migration in frozen medium and characterises to some extent the dissolving properties of the film.

The transport of copper ions in the liquid-like film from the frozen substrate to the snowcover is evident. But the copper ion concentration in snow differs by two orders of magnitude compared to the ions of the background electrolyte (sodium chloride), although the initial concentration of copper ions is only one order of magnitude less than that of sodium ions. This is probably due to the specific behaviour of copper ions in a frozen medium.

Sodium ions and chloride ions provide examples of the specific features of ionic migration under these conditions. The concentration ratio of Na⁺ ions to Cl⁻ ions in the snow layer before snow-melt suggests that cation migration is impeded. The content of Cl ions in the snow is several times that of Na⁺ ions, although their ratio in the initial solution is 1.4. The similar ratio $(5.4 \cdot 10^{-4}/3.97 \cdot 10^{-4} \text{ mole/l})$ of these ions is reached in the snow when the temperature approaches 0°C (6 May 1995) and the liquid-like film thickness is at least several tens of nanometers (Kvlividze et al. 1974). Considering the unsteadiness of the film thickness under the transient temperature regime (Fedoseyeva & Nechaev 1984), one would expect still greater thicknesses and correspondingly the physicochemical characteristics closer to those of bulk solution.

The lesser mobility in the film of Na⁺ ions relative to Cl^- ions under the conditions considered may be attributed to the greater degree of cation hydration (Sinyukov 1976) observed in ordinary solutions. Presumably, the specific structure of the liquid-like film which differs from that of bulk solution (Ushakova 1975) also contributes to the difference in interaction with water molecules at subzero temperatures. A temperature decrease and associated increase in medium's viscosity together deteriorate the properties of pore solution as the medium for migration. It is worth noting that the diffusive characteristics of the ions ²²Na⁺ and ³⁶Cl⁻ estimated from the results of migration studies in natural conditions of Antarctica (Ugolini & Anderson 1972) differed by more than one order of magnitude.

5 CONCLUSIONS

The results of the investigations reported here, as well as those of the experimental study of gold migration (Fedoseyeva & Fedoseyev 1991) indicate that the upward movement of solutes into snow along the liquid-like film already occurs at temperatures of 12-13°C below zero. Because of relatively low temperatures in the snowcover during the observation period and some inertia of the liquid-like film with respect to this factor (Fedoseyeva & Nechaev 1984), the daily temperature amplitude in the examined snow layer in this period is not significant to change the liquid-like phase content. However a moisture gradient under the changing temperature regime can have a significant effect (Fedoseyeva et al. 1986, Fedoseyeva 2000). The liquidlike film thickness increases with further warming of the snowcover (Kvlividze et al. 1974), facilitating solute migration from the substrate.

It is evident that the surface film of ice plays a role in solute migration in the glacial system. The results obtained indicate the importance of the liquid-like film on disperse ice inclusions for concentration diffusion of solutes in frozen soils as well. Theoretical investigations of disperse ice are needed to improve understanding of the characteristic properties of the surface film and its role in migration of chemical species in frozen media.

When analysing the results and formulating the conclusions, we are aware that these results have been obtained with some assumptions; the main assumption is that the liquid-like phase content and the ionic concentrations are averages for the observation period. However the qualitative conclusion on the importance of the liquid-like film in solute migration in frozen systems appears to be reasonable.

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