The present paper deals with the problem concerning peculiarities of mineral transformations in permafrost-affected soils (cryosols) influenced by permafrost table and its relief.

It was shown that soil formation in cryosols results in visible transformations of mineral mass as a consequence of some specific properties such as acid pH, humus composition, contrast redox conditions. Freeze-drying of soil material results in sharp changes in redox conditions, concentration of pore solutions, coagulation and crystallization of mineral phases (Naumov, Gradusov, 1964, 1974; Zvereva et al, 1983, 1992). Main trends of mineral transformations in this soils have been described. At the same time little is known, however, about mineral Fe behavior in cryosols. Moessbauer spectroscopy data and magnetic measurements allowing to confirm morphologically observing mobility and proposed synthesis of Fe-compounds in this soils have not been present in literature up to now.

The sites under study are situated on the middle Bolshaya Chukochya River (North Kolyma Lowland, North-Western Siberia, Russia). Soils studied are developed from Yedoma (Q$_3^{2-4}$) deposits. The chosen sites had a relatively low degree of morphological variability and were more or less homogeneous both inside the soil profiles and in the upper part of perennially frozen sediments. Deposits are present by loamy sand material of yellowish, olive and brownish colors with inclusions of coarse humus and plant roots. Diffusive black, brown and reddish spots and microconcreations are observed. The soil surface represents an alternation of hillocks of irregular shape of 3.5-5 m in a diameter and 20-35 cm height. The surface of hillocks is partly covered predominantly with moss vegetation lined with hardly decomposed peat layer up to 25 cm thick.

The actual thickness of the thawed layer at the date of its measurement (August 5, 1994) was within 0-32 cm. According to the results of direct one-week observations it was increasing with a mean rate of about 2 mm/day. The depth of thawing was minimal at sites with a thick peat or moss cover where a portion of this cover was preserved in the frozen state. The maximal thawing of soil was revealed under the vegetation-devoid sites on the surface of hillocks. As a result of irregular thawing with a depth, the surface of the thawed layer (permafrost table) is presented by bulges and cauldrons with planar
diameters of 1.2 - 2.5 m. In the depressions of the permafrost table relief the thawed soils were saturated with water.
16 mixed samples which characterize zones definitely different from neighboring ones by their cryogenic structure and other morphological properties have been taken for the investigation. In other words, samples from two soil profiles including the material from permafrost zone which occupy the highest and lowest parts of the microrelief have been taken.
The mineralogical analyses of clay (<2 µm) fraction of samples were carried out by X-ray diffractometry using CuKα radiation. The specimens were step-scanned between 2° and 35° 2θ using 0.1° and 0.05° 2θ increments with 5 sec counting time. Clay fraction was separated from samples by sedimentation after dispersion in water paste. Mg-saturated slides were X-rayed at room temperature, after ethylene-glycol salvation and heating to 300° and 550° C. Oriented specimens were prepared by sedimentation on glass slides of 25x25 mm of aliquots (20 mg) of Mg-saturated material. The iron compounds were studied by Mössbauer spectroscopy and magnetic measurements. The Mössbauer spectra were recorded with MS1101-E spectrometer with a constant-acceleration drive system (57Co/Cr source with an activity of about 32mCi). The velocity scale was calibrated with reference to sodium nitroprusside and metallic Fe. The specific magnetic susceptibility was measured with a Kappabridge KLY-2 instrument. The thermo-magnetic determination of lepidocrocite was followed the Vodynitskii Y.N. procedure (1989) which is based on the transformation of the slightly magnetic γ-FeOOH into the highly magnetic maghemite γ-Fe2O3 under heating at 300 - 350°C.

Figure 1. Clay mineralogy distribution (% in clay fraction)

The clay fraction of Yedoma deposits is enriched by hydromica (55-75 %). Besides, the following mineral phases are present: Fe-Mg chlorite (25-40 %), irregular interstratified mica-smectite (content of smectite phase varies in 3-10 %), Mn-calcite (traces). (Fig.1)
Two main processes of clay minerals transformations within the zone of periodic seasonal thawing (active layer) are observed: dissolution of chlorite and degradation of mica with irregular interstratified mica-smectite formation. The intensity of this processes depends on a position in the soil profile and the relation to the relief of permafrost table. The highest degree of transformations takes place in the depression of the permafrost table and upper mineral horizon. The content of smectite phase in this layers is up to 10% in a comparison with 4-5% in the material from permafrost zone. Mica degradation with K releases as a consequence of freezing-thawing and wetting-drying was mentioned in literature (Goulding, 1986; Robert, 1986). Degradation could be caused by frequent temperature and redox fluctuations playing a role of a so-called "chemical crusher" which is especially contrasting close to the permafrost table and on the soil surface.

Dissolution of chlorites occurs in the upper mineral horizon of a soil developed on the hillock where its content reduces from 35-40% in the permafrost zone to 20%.

Fe-Mg chlorites are unstable under soil formation and their dissolution is a common soil process taking place in many soil types including cryosols (Sokolov et al, 1978, 1981).

The Mössbauer spectra obtained at temperature 298 K and 900 K represent the superposition of lines of Fe²⁺ and Fe³⁺ which occupy different structural positions in the mineral components of sediments. High Fe²⁺/(Fe²⁺ + Fe³⁺) ratio - 30-40% (up to 50%, in freeze sediments) reflects the low intensity of weathering. Fe²⁺ occupies the structural positions in chlorite and hydromica.

In an active layer the reduction of a Fe²⁺ in structure of silicates and significant (twice) increase of Fe in clay fraction on the boundary with permafrost zone are observed. The analysis of Fe distribution was based on Mössbauer spectroscopy data. The iron concentration in a test sample is proportional to the area under the spectral curve standardized for the background and equal sample mass.

Goethite, hematite and other hydroxides have not been observed by means of Mössbauer spectroscopy. - the lines of sextet in the spectra are absent. The results of thermomagnetic analysis demonstrate the presence of lepidocrocite. The maximal concentration of lepidocrocite - till 0.34% from weight of a sample in an clay fraction.
and 0.16 % for a sample as a whole, are observed at the permafrost table. (Fig. 2). In a permafrost zone concentration of lepidocrocite is visibly lower - 0.01-0.03%. Lepidocrocite, the second most abundant form of FeOOH, is less stable than goethite and occurs mainly in soils. Overmoistered soils and gleyed horizons are the most enriched in lepidocrocite. The formation of lepidocrocite requires an adequate amount of Fe$^{2+}$ in solution. It is mainly abundant in clay noncalcareous soils with periodical and local anaerobic conditions. Not only the reduction stage, but also the slow oxidation of Fe$^{2+}$ (i.e. oxidation stage) is the important factor for its formation. (Schwertmann, 1989, 1993; Vodynitzkii, 1989; Alekseeva 1997)

The similar conditions, necessary for lepidocrocite synthesis, are observed in an active layer. As a result of the seasonal dynamics of temperature, moisture, pH, Eh, the highest concentration of lepidocrocite in the bottom of active layer takes place. The high content of

Figure 2. Lepidocrocite distribution in clay fraction (% from sample mass).
Figure 3. Magnetic susceptibility distribution (*10⁶ SI)
a-clay fraction; b- bulk sample

lepidocrocite on the boundary with permafrost in micro depression of cryopedon probably connects with higher organic substances content and more contrast dynamics of conditions with periodic drying-moistening.

The samples studied are very weakly magnetic (10-30*10⁶ SI). The clay fraction has a lower magnetic susceptibility than the soil as a whole (5-10*10⁶ SI) (Fig.3). The formation of the dispersed magnetics does not occur in active layer. Particles of paramagnetics contribute greatly to a susceptibility, and, therefore, an increase of magnetic susceptibility is associated with an increase of iron compounds content, e.g. - Fe-chlorites.

Conclusions
Mineralogical composition of soil studied are determined by hydromica-chlorite association of Yedomic deposits, climate conditions (extremely cold and dry) and permafrost influence. All this peculiarities cause extremely weak chemical weathering of soil material and its mainly inherited origin.

Degradation of hydromica, weathering of Fe-containing minerals (chlorite) with further iron migration within active layer and crystallization on the cryogenic barrier in the form of lepidocrocite are the main processes of mineral transformations in cryosols studied. The highest concentration of lepidocrocite is connected with the boundary of permanently frozen ground.

The received results in a complex with other data allow to note that geochemical processes are strongly influenced by the closed-surface permafrost table and its relief. The boundary between the seasonally thawing soil and the permanently frozen ground could be regarded as an important geochemical barrier - Frozen Geochemical Barrier.
Keywords: permafrost, cryosol, clay mineralogy, iron oxides
Mots clés: pernagel, crysol, argile minéralogique, oxyde de fer