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Calcium Oxalates in Soils within Disturbed Landscapes and Rock on the Territory of Yakutia (Russia), Formation Conditions in a Sharply Continental Cryoarid Climate

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Abstract: The formation of oxalates in soils and rocks under conditions of cryoarid climate, permafrost and taiga vegetation was studied. Whewellite and weddellite were found in four areas associated with the mining industry: on the kimberlite deposit of the Daldyn territory, in the lower reaches of the Markha River of the Central Yakut Plain, and on the coastal outcrop of the Allah-Yun Sellah-Khotun ore cluster. Whewellite was found in the upper organic horizon of Skeletic Cryosol (Thixotropic) (sample 151) and as a film on the surface of plant remains of Humic Fluvisols (sample 1663). Weddellite was found as an extensive encrustation on the surface of the soil and vegetation cover of Stagnic Cryosols Reductaquic (sample 984) and on a siltstone outcrop (sample KM-6-21). Calcium oxalates were identified by X-ray phase analysis, photographs of the samples were taken on a polarizing microscope, and the crystal morphology was studied on a scanning electron microscope. To determine the chemical composition of soils and rocks, the classical wet-chemical method was used; the physical properties of the studied samples were studied using a pH meter, the photoelectric colorimetric method, and a synchrotron thermal analysis device. The source of calcium for the formation of salts is the parent layers of the studied soils, represented by carbonate and carbonate clastic rocks, which cause neutral and slightly alkaline environments. High humidity, which is provided by the seasonal thawing of the permafrost, has a key role in the formation of the studied oxalates in Yakutia with a sharply continental cryoarid climate. Based on the studies, it was found that the first two samples are the products of lichen activity, and the third and fourth are at the stage of initial soil formation by micromycetes. In addition, the formation of these oxalates, in our opinion, is the result of the protective function of vegetation, in the first two cases, with a sharp increase in the load on lichens under technogenic impact, and in the second and third cases, when favorable conditions arise for initial soil formation, but under conditions of toxic content of heavy metals and arsenic.

Keywords: biomineralization; weddellite; whewellite; Cryosol; Fluvisol; siltstone; lichens; micromycetes

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Citation: Vasileva, T.I.; Legostaeva, Y.B. Calcium Oxalates in Soils within Disturbed Landscapes and Rock on the Territory of Yakutia (Russia), Formation Conditions in a Sharply Continental Cryoarid Climate. *Minerals* **2023**, *13*, 659. https://doi.org/10.3390/min13050659

Academic Editors: Oluwatoosin Agbaje and Olev Vinn

Received: 18 March 2023
Revised: 25 April 2023
Accepted: 8 May 2023
Published: 10 May 2023

1. Introduction

Biomineralization is central to geomycological processes, including the circulation of nutrient materials, transformation of rocks, minerals and metals, bio-weathering and mycogenic mineral formation [1,2]. At present, there are about a hundred biominerals of various genesis, with oxalates being one of the representatives. They are quite widespread in nature and in the human body; the most common of the oxalates are calcium oxalates: whewellite—$Ca(C_2O_4){\cdot}H_2O$ and weddellite—$Ca(C_2O_4){\cdot}2H_2O$. The third unstable form—caoxite $Ca(C_2O_4){\cdot}3H_2O$—is extremely rare [3,4].

They have been found in calcium oxalates in higher and lower plants of Scotland, Italy, Israel, Mexico, Bulgaria, Morocco, France, Australia, and other countries [5–12]. Note the oxalate findings in the extreme environment of Antarctica: (i) in the sediments of the

Weddell Sea in the form of minuscule, colorless tetragonal crystals—"envelopes" [13], (ii) in microbial communities in areas with a predominance of the first lichens (cryptoendolites) in the Ross Desert, which exist due to the solar heating of the rock surface and microscopic greenhouse conditions during the melting of snowfalls [14]. It is essential to note that most of the published works describe the formation of oxalates in tropical, subtropical, and very rarely in arid climates.

In Russia, the findings of calcium oxalates were discovered in the following areas: in the Leninskaya formation in Kuzbass, which was formed in alluvial, basin, and bog environments [15]; on the marble and limestone surfaces of buildings and monuments in Crimea [16]; in quartz-carbonate Pb-Zn veins of the Murmansk coast; in the Kolsky region [17]; on the surface of apatite-nepheline rocks of the Khibiny alkaline massif [18]; and in lichen thalli on scoria cones of Tolbachik volcano on the Kamchatka Peninsula [19]. In Yakutia, two oxalate findings were recorded in the brown coal mines of the Tyllakh and Chai-Tumus deposits (the left bank of the Olenkhinsky channel and the mouth of the Lena River, Bulunsky district). This finding was described by P.I. Glushinsky [20] as stringers in brown coal saturated in the permafrost zone, associated with calcite and dolomite. Other oxalates have also been found there—glushinskite, stepanovite, zhemchuzhnikovite [21]. We have described and studied in detail weddellite, found in the form of an extensive plaque in the Daldynsky kimberlite field [22].

The role of calcium oxalates in plants and fungi is still very much under discussion. Typically, the formation of oxalates is associated with the carbon cycle and vital activity of plants [23–25]. Some authors suggest that the primary function of the biosynthesis of Ca-oxalate is the regulation of ionic equilibrium and osmotic pressure in cells [26,27]. Others believe that it is essential for controlling the calcium and oxalic acid concentrations [28–30]. Still, others accept that the formation of oxalates is a means of essential ion preservation that is either confined to the mechanical support and protection of plants or to the exclusion of metals and reduction of their toxic effects [31,32].

The objective of our research is to describe the oxalate findings and to analyze the geochemical specifics of the calcium oxalate formation in soils and rocks that occurred under the conditions of hyper-continental climate, permafrost, and taiga vegetation.

2. Materials and Methods

During a five-year study of the geoecological conditions in the mining regions of Yakutia, among more than two thousand sampling points, only four points were identified to contain calcium oxalates that were formed during the interaction of vegetation with soil minerals and rock (Figure 1).

2.1. Characteristics of Oxalate Formation Sites

Two samples were collected on the territory of the Udachninsky Mining and Processing Plant of PJSC ALROSA in the Daldyn kimberlite field, the Anabar anteclise. The first sample (sample 151) was found in the upper horizon of Skeletic Cryosol (Thixotropic) at the top of the watershed, in the southwestern part of the Udachny (66°23′44.9′′ N, 112°11′53.3′′ E). The second sample (sample 984) was found in a microdepression on the ground cover surface of the Stagnic Cryosols Reductaquic, 1.5 km to the north of the tailing dump (66°24′00.0′′ N, 112°17′00.0′′ E).

The third sample (sample 1663) was found on the border of vegetation and the upper organic horizon of Humic Fluvisol alluvial soils in the area of the lower reaches of the Markha River (left tributary of the Vilyui River) in the Central Yakutian lowland, the Vilyui syneclise (63°32′48.56′′ N, 118°20′03.72′′ E).

The fourth sample (sample KM-6-21) was found on the coastal outcrop of the Allakh-Yun River of the gold deposits of the Sellyakh-Khotun ore node of the Allakh-Yun metallogenic zone, the South-Verkhoyansk synclinorium (61°04′08.08′′ N, 138°04′31.35′′ E).

Figure 1. Overview map of the study area location: 1—territory of Daldyn kimberlite field, samples 151 and 984; 2—territory of Markha River in the Central Yakutian lowland, sample 1663; 3—territory of Allakh-Yun River in the Sellakh-Khotun ore cluster, sample KM-6-21.

2.2. Natural and Climatic Conditions

The climate of Yakutia is sharply continental, characterized by hot, short, dry summers with high insolation and long, extremely harsh, low-snow winters. Due to the extreme continentality of the climate, there are large temperature fluctuations between winter and summer (the absolute annual amplitude of the air temperature is 95 °C), and between daytime and night-time (average amplitude of air temperature 15 °C), especially in autumn and spring [33]. The territory is located in the permafrost zone, which, according to the National Snow and Ice Data Center, has the largest thickness in the world [34].

The Daldyn kimberlite field (Anabar anteclise) is composed of deposits of the Lower Paleozoic. They are represented by homogeneous strata of carbonate rocks of the Morkoka formation (upper division of the Cambrian system)—$\in_3 mr$ and the Oldonda formation (lower division of the Ordovician system)—$O_1 ol$ (limestones, dolomite limestones, dolomites), soft quaternary strata and igneous rocks of the tholeiitic basalts, as well as ultrabasic rocks—kimberlites [35,36]. The territory of the Daldyn kimberlite field, due to a rather warm but short summer and very low winter temperatures, has a negative average annual temperature (−13.3 °C), which leads to a favorable environment for the preservation of the permafrost. Permafrost is widespread, and the thickness of the active layer, depending on the exposure of the slopes and their forest cover, ranges from 0.2 to 1.5 m. Therefore, in conditions of low humidity, high summer temperatures, and insufficient precipitation (247 mm), the summer thawing of the permafrost contributes to the constant soil moistening. Thus, the mottled and bumpy cryogenic microrelief with a well-marked permafrost cracking is pronounced in the territory. The territory is located in the subzone of open larch woodland taiga of Larix dahurica; dwarf shrubs are represented by the lean birch

Betula exilis, alder Alnus fruticosa, black crowberry Empetrum nigrum, and wild rosemary Ledum palustre [37].

The Central Yakutian lowland (Vilyui syneclise) is composed of alluvial deposits of inequigranular sands of the Karginsky and Sartan horizons of the Quaternary system (Q_4), and sandstones of quartz–feldspar composition with carbonate cement of the Yakut formation of Jurassic deposits ($J_{1\text{-}2}sn$) [38]. The average annual air temperature of the territory is negative (up to −11.1 °C). The annual amount of precipitation varies from 257 to 354 mm [33]. The low average annual temperature of rocks in relation to the negative radiation balance leads to the frost penetration of the upper horizons of the lithosphere and the formation of permafrost strata, with a thickness of 400–700 m. Permafrost is widespread, and the thickness of the active layer on the Lena–Vilyui plain is 0.2 m [39]. The vegetative cover is formed by middle taiga larch forests with Larix dahurica mixed with Picea obovata, reed-sedge bogs and forbs-grass, and often salt meadows, while willow Salix rossica predominates in plant communities of the rivers and lakes [40].

Bank sediments of the Allah-Yun River of the Sellakh-Khotun ore cluster (South-Verkhoyansk synclinorium) is represented by interstratified beds of calcareous sandstones and siltstones of the Surkechan formation of the Upper Carboniferous (C_3sr_1). The climate of the southwestern part is sharply continental with contrasting differences of summer and winter temperatures ranging from +35 °C to −60 °C. The average annual air temperature over the past 5 years was −12.2 °C [41]. The annual precipitation is 400–500 mm, primarily occurring in July–August. Permafrost rock in the coastal part of the territory is discontinuous and insular in distribution, with a thickness ranging from 5 to 70 m. The active layer thickness on the slopes of the southern exposure reaches 3–5 m, and decreases to 1–0.3 m in the north. The watershed slope vegetation is developed in the form of larch Larix dahurica, cedar elfin Pinus pumila, wild rosemary Ledum palustre, and dwarf birch Betula nana with a moss-lichen cover of varying degrees of density [42].

2.3. Objects of Research

The objects of study are calcium oxalates and the conditions for their formation. In the aspect of research, soils and rocks are components of the ecosystem on which oxalates are formed at the boundary between the vegetation cover and the upper organogenic horizon. According to the classification system of the IUSS WRB working group [43], soil profiles were classified as Skeletic Cryosol (Thixotropic) (Figure 2a), Stagnic Cryosol Reductaquic (Figure 2b), and Humic Fluvisol (Figure 2c), respectively. The rock is represented by siltstone (Figure 2d).

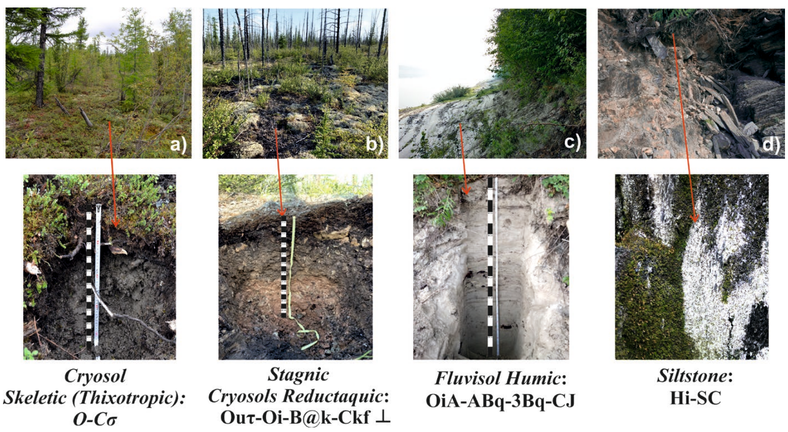

Figure 2. Photo of general view of study area, soil profiles and denudation: (**a**) crowberry–blueberry larch woodland, moss-lichen cover, Skeletic Cryosol (Thixotropic) soil cover, (**b**) technogenically transformed larch forest with moss-lichen cover, Stagnic Cryosols Reductaquic soil cover, (**c**) bank of the Markha River, with alder–rosehip grass vegetation, Humic Fluvisol soil cover, and (**d**) outcrop on the Allakh-Yun river, composed of siltstone.

2.4. Research Methods

Coating, soil material, and rocks were analyzed at the Multiple-access Center of the Diamond and Precious Metal Geology Institute, Siberian Branch, Russian Academy of Sciences (Yakutsk) (MAC DPMGI SB RAS) and Arctic Innovation Center of the North-Eastern Federal University (Yakutsk) (AIC NEFU). The classical wet chemical method was used to determine the chemical composition of soil [44,45] (analysts L.T. Galenchikova, A.S. Vasilyeva).

The soil pH was measured in soil–water suspension (1:2.5) at room temperature using a Seven Compact Advanced pH meter (Mettler Toledo, Greifensee, Switzerland) according to the state standard [46,47]. The photoelectric colorimetric method (KFK-2 UHL 4.2 Russia) was used to identify soil organic carbon (SOC) according to the state standard [48,49] (MAC DPMGI SB RAS, analyst A.N. Nikolaeva).

Identification of calcium oxalates and determination of the mineralogical composition of soils was performed by X-ray phase analysis on the D2 PHASER diffractometer (Bruker, Karlsruhe, Germany). The samples were shot on a tube with a copper anode (CuKα), at a voltage of 30 kV and a current strength of 10 mA, with a step of 0.05°, a shooting interval of 4.5–65° (2θ°), rotation of 30 rpm, and exposure of 1 s at a point. The PDF-2 database was used.

The sample photographs were taken on a MT9430L polarization microscope of (Meiji Techno, Saitama, Japan) by M.V. Kudrin (DPMGI SB RAS).

Crystal morphology was studied on a JEOL JSM-7800F electron scanning microscope (JEOL Ltd., Tokyo, Japan) with Oxford X-MAX-20 energy dispersion spectrometer, accelerating voltage 2 kV (AIC NEFU, analyst A.A. Diakonov), and on a JEOL JSM-6480LV (JEOL Ltd., Tokyo, Japan) with energy dispersion spectrometer Energy 350 Oxford, accelerating voltage 20 kV, probe current 1 nA (MAC DPMGI SB RAS, analyst A.V. Popov).

Thermogravimetric characteristics of the studied samples were identified on an NETZSCH-STA 449C Jupiter (NETZSCH, Selb, Germany) synchrotron thermal analysis device. The samples in powder form were heated from room temperature to 1000 °C at a heating rate of 10 S/min in an inert argon medium (MAC DPMGI SB RAS, analyst N.N. Emelyanova).

3. Results

The main parameters of the chemical and mineralogical composition of the samples are presented in Tables 1–3.

Table 1. Chemical composition and mineral compounds of the Cryosols without oxalates and with oxalates.

	Cryosol Nature				Cryosol with Oxalates in the Organic Horizon					
Section	**Skeletic Cryosol (Humic) (Sample 1181)**				**Skeletic Cryosol (Thixotropic) (Sample 151)**		**Stagnic Cryosol Reductaquic (Sample 984)**			
Depth, cm	0–9 (10)	9 (10)–14 (18)	14 (18)–23 (46)	23 (46)–49	0–6 (9)	6 (9)–38	0–1 (3)	1 (3)–13 (16)	13 (16)–33 (41)	33 (41)–61
SiO_2, %	6.24	49.13	19.82	39.48	46.93	41.94	5.43	3.50	40.52	35.70
Al_2O_3, %	1.19	10.23	4.74	8.36	11.39	10.69	0.79	1.40	7.83	8.78
Fe_2O_3, %	0.45	1.83	3.49	2.48	4.84	4.84	1.03	0.52	0.05	3.02
K_2O, %	0.48	3.90	1.52	3.39	4.34	4.18	0.32	0.38	3.05	3.40
Na_2O, %	0.02	0.22	0.02	0.13	0.23	0.16	0.24	0.02	0.17	0.09
CaO, %	1.36	6.81	5.34	12.41	4.72	13.7	8.96	6.42	10.57	12.98
MgO, %	0.68	6.66	1.78	10.13	3.07	5.35	0.91	1.05	8.21	10.91
MnO, %	0.01	0.07	0.04	0.05	0.10	0.05	0.02	0.01	0.09	0.06
CO_2, %	1.88	9.57	1.86	18.73	2.23	13.42	1.57	1.13	14.91	19.76
PPP, %	64.39	4.72	53.98	18.73	16.85	4.38	66.62	73.88	14.91	19.76
pH	6.2	7.8	7.4	7.9	6.5	7.2	7.8	7.4	7.8	7.8
SOC, %	>30	6.34	0.22	1.80	11.10	1.50	23.80	20.20	6.10	1.80
Mineral compounds	Quartz Dolomite	Quartz Dolomite Feldspar Chlorite Mica	Quartz Dolomite Feldspar Chlorite Mica	Dolomite Quartz Feldspar Chlorite Mica	Quartz Feldspar Whewellite Chlorite Mica Calcite	Quartz Feldspar Dolomite Calcite Mica Chlorite	Weddellite Quartz Calcite Dolomite	Quartz	Quartz Dolomite Feldspar Chlorite Mica	Dolomite Quartz Feldspar Chlorite Mica

Note: here and below SOC—soil organic carbon.

Table 2. Chemical composition and mineral compounds of the Fluvisols without oxalates and with oxalates.

	Fluvisol Nature						Fluvisol with Oxalates in the Organic Horizon							
Section	**Humic Fluvisol (Sample 1671)**						**Humic Fluvisol (Sample 1663)**							
Depth, cm	0–10	10–20	20–30	30–58	58–91	91–131	0–2	2–10	10–15(20)	15(20)–23(25)	23(25)–27(30)	27(30)–75(78)	76(78)–110	110–195
SiO_2, %	71.12	72.45	72.19	71.05	70.01	69.42	2.36	64.64	69.97	69.36	68.98	72.15	73.2	73.52
Al_2O_3, %	12.14	11.99	11.04	10.64	10.09	11.6	0.44	14.28	15.94	15.95	16.31	15.26	14.88	14.65
Fe_2O_3, %	0.95	1.14	1.04	1.24	1.85	1.67	1.13	1.15	0.41	0.54	0.65	0.29	0.4	0.16
K_2O, %	3.03	3.08	2.95	2.70	2.54	2.91	0.04	3.34	3.79	3.75	3.82	4.29	3.94	3.98

Table 2. *Cont.*

	Fluvisol Nature						**Fluvisol with Oxalates in the Organic Horizon**							
Section	**Humic Fluvisol (Sample 1671)**						**Humic Fluvisol (Sample 1663)**							
Na_2O, %	2.74	2.85	2.67	2.27	2.14	2.60	0.03	2.97	3.45	3.51	3.5	4.03	3.79	3.77
CaO, %	2.53	2.43	2.81	3.33	3.64	2.73	4.08	3.63	1.63	1.72	1.74	1.71	1.66	1.72
MgO, %	0.93	1.15	0.94	1.75	2.63	2.31	0.15	1.37	0.06	0.22	0.33	0.08	0.15	0.15
MnO, %	0.04	0.03	0.05	0.05	0.07	0.04	0.02	0.03	0.01	0.01	0.01	0.01	0.01	0.01
CO_2, %	0.74	0.51	0.34	1.09	1.06	0.88	0.22	2.23	0.19	0.16	1.26	0.06	0.40	0.10
PPP, %	2.44	1.96	1.91	2.11	1.05	2.08	90.57	3.55	2.88	2.92	1.72	0.62	0.48	0.65
pH	6.9	6.9	7.3	7.4	7.1	7.1	6.5	6.9	6.9	6.9	6.7	6.8	6.8	6.8
SOC, %	1.64	1.32	1.29	1.42	0.71	1.41	25.9	2.40	0.90	1.20	1.20	0.10	0.10	0.10
Mineral compounds	Quartz Feldspar Dolomite Montmorillonite Mica	Quartz Feldspar Dolomite Montmorillonite Mica	Quartz Feldspar Dolomite Montmorillonite Mica	Quartz Feldspar Dolomite Montmorillonite Mica	Quartz Feldspar Dolomite Montmorillonite Mica	Quartz Feldspar Dolomite Montmorillonite Mica	Whewellite Quartz	Quartz Feldspar Dolomite Montmorillonite Chlorite Mica	Quartz Feldspar Montmorillonite Chlorite Mica	Quartz Feldspar Montmorillonite Chlorite Mica Mica	Quartz Feldspar Dolomite Montmorillonite Chlorite	Quartz Feldspar Chlorite Mica	Quartz Feldspar Mica	Quartz Feldspar Chlorite Mica

Table 3. Chemical composition and mineral compounds of the siltstone without oxalates and with oxalates.

Section	Siltstone (Sample XYu-1-21)	Siltstone with Weddellite (Sample KM-6-22)
SiO_2, %	60.57	58.29
Al_2O_3, %	15.64	21.23
Fe_2O_3, %	6.88	7.59
K_2O, %	2.69	7.35
Na_2O, %	1.88	2.31
CaO, %	0.77	0.20
MgO, %	2.06	1.53
MnO, %	0.03	0.10
CO_2, %	0.97	0.10
PPP, %	5.78	0.10
pH	7.3	6.1
SOC, %	1.35	3.60
Mineral compounds	Quartz Feldspar Mica Chlorite	Quartz Feldspar Weddellite Chlorite Mica

The amount of CaO in the upper soil horizons is not related to the calcite content, as the quantity of CO_2 in the same horizons is significantly lower. Probably, the increase in the amount of CaO is associated with soil organic carbon. All soils and rocks have a neutral or slightly alkaline medium, with a pH ranging from 6.1 to 7.8. The SOC content of soils is sufficiently high; the organic matter is mostly of coarse humus composition, and the SOC content in siltstone is explained by the penetration of small remnants of moss-lichen cover into the sample. When comparing soils and rocks containing oxalates with soils and rocks from the same environment that do not have oxalates, no clear differences could be found. The primary minerals of the parent rock of Skeletic Cryosol (Thixotropic) and Stagnic Cryosol Reductaquic are quartz, feldspar, dolomite, calcite, mica, and chlorite. Humic Fluvisol consists of quartz, feldspar, dolomite, montmorillonite, chlorite, and mica. The minerals composing siltstone are quartz, feldspar, chlorite, and mica. Thus, the sources of calcium for lichens are probably the carbonates of the Oldonda (O_{1ol}) and the Morkoka ($\in_{3mr}$) formations of the Cambrian and Ordovician, of the Suntar Formation ($J_{1\text{-}2\,sn}$) of Jurassic deposits for micromycetes of Humic Fluvisol, and calcareous sandstones of the Surkechan Formation (C_{3sr1}) of the Upper Carboniferous deposits for siltstone.

Calcium oxalates were detected only in surface samples taken from organo-mineral horizons at the vegetation boundary. Weddellite was detected in the Daldyn kimberlite field soil at the top of the watershed of the interfluve of the Svetly and Chuzhoy streams, and the rocks of the coastal outcrop of the Allakh-Yun River (Table 1 and Figure 3b,d). Whewellite was detected in samples 1.5 km north of the 1 stage tailings dump and the lower reaches of the Markha River (Table 1 and Figure 3a,c). In the first case, weddellite is associated with quartz, feldspar, calcite, and dolomite; in the second—with quartz, feldspar, mica, and chlorite. Whewellite is associated with quartz, dolomite, feldspar, chlorite, and mica. In sample 1663, only quartz was detected together with whewellite, since the upper horizon consisted solely of alder plant litter and semi-decomposed organic matter.

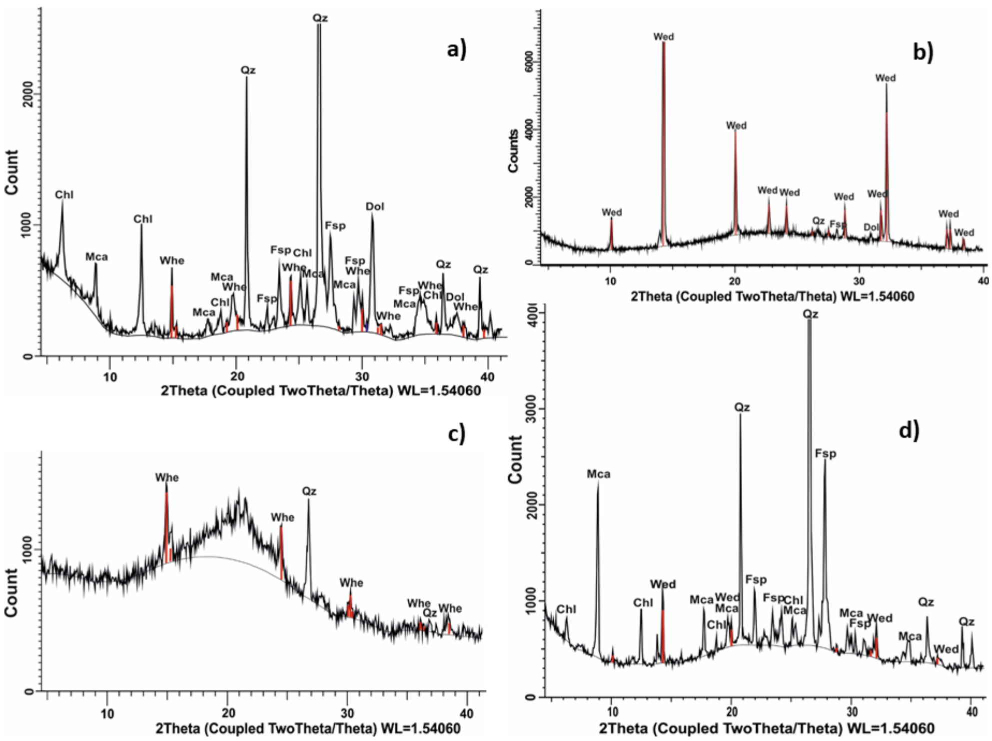

Figure 3. Powder X-ray diffraction patterns: (**a**) upper soil horizon of the Daldyn kimberlite field, sample 151; (**b**) cover on soil of Daldyn kimberlite field, sample 984; (**c**) plant litter on the Markha riverbank, sample 1663; and (**d**) siltstone cover of outcrop on the Allakh-Yun River, sample KM-6-2. Abbreviations [50]: Wed—weddellite, Whe—whewellite, Qz—quartz, Fsp—feldspar, Mca—mica, Chl—chlorite, Dol—dolomite.

The appearance of the selected samples and micrographs revealed that the samples 151, 984 and KM-6-21 are fine-grained fragments. Sample 1663 is represented by weakly decomposed organic material, which is covered by a mineral crust consisting of whewellite (Figure 4e,f). Dipyramidal weddellite was detected in sample 984 (Figure 4c,d). Whewellite in sample 1663 (Figure 4e,f) and weddellite in sample KM-6-21 (Figure 4g,h) are probably represented as prisms.

Thermogravimetric analysis showed that endothermic effects observed in the sample are associated with the release of hygroscopic and chemically bounded water, as well as the breakdown and dissociation of carbonates, and with the gradual breakup of minerals, including oxalates [51,52]. Exothermic effects are associated with the combustion of various plant residues typical of the bonitet of the studied area [53,54]. Whewellite (Figure 5a) was detected in the upper organic horizon of Skeletic Cryosol (Thixotropic) and in the form of a film on the surface of plant residues of Humic Fluvisols (Figure 5c); therefore, there is a distinct exothermic effect in the range of 200–400 °C associated with the combustion of organic matter [54]. The additional endothermic effect in the samples taken on the Stagnic Cryosol Reductaquic (sample 984) (Figure 5b), Humic Fluvisols (Figure 5c), and siltstone (sample KM-6-21) (Figure 5d) in the area of 200–600 °C is probably related to the presence of other components (for example, iron hydroxides typical of soil and oxidized outcrops), not detected by XRD (Figure 3b–d), possibly due to their amorphous character [53].

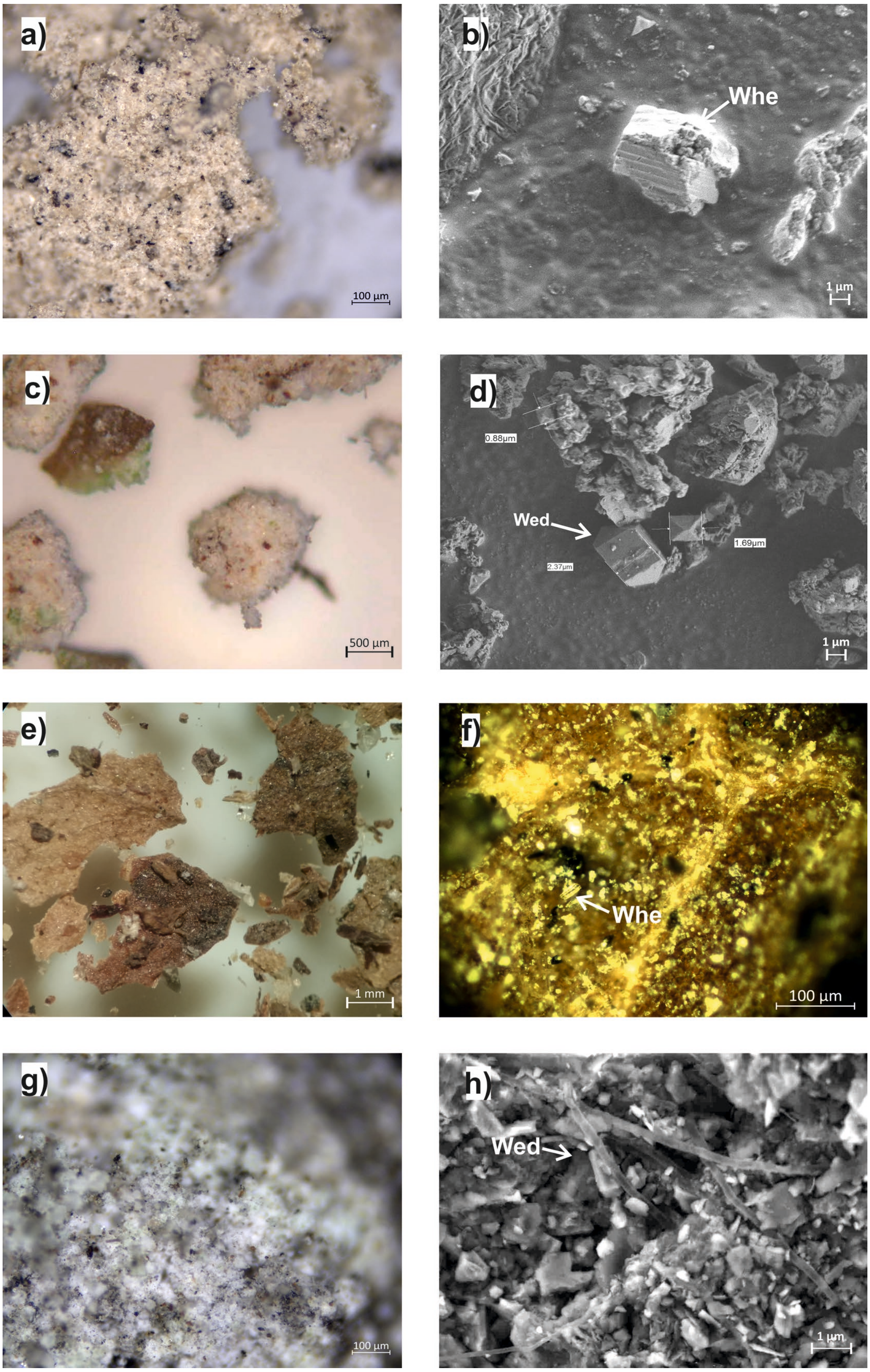

Figure 4. Photo of coatings (**a**,**c**,**e**,**g**) and scanning electron microscopic images (**b**,**d**,**f**,**h**): in samples of the upper soil horizon, sample 151 (**a**,**b**); coating on the soil, sample 984 (**c**,**d**); plant litter on the bank, sample 1663 (**e**,**f**); and coating on the siltstone of the outcrop, sample KM-6-21 (**g**,**h**).

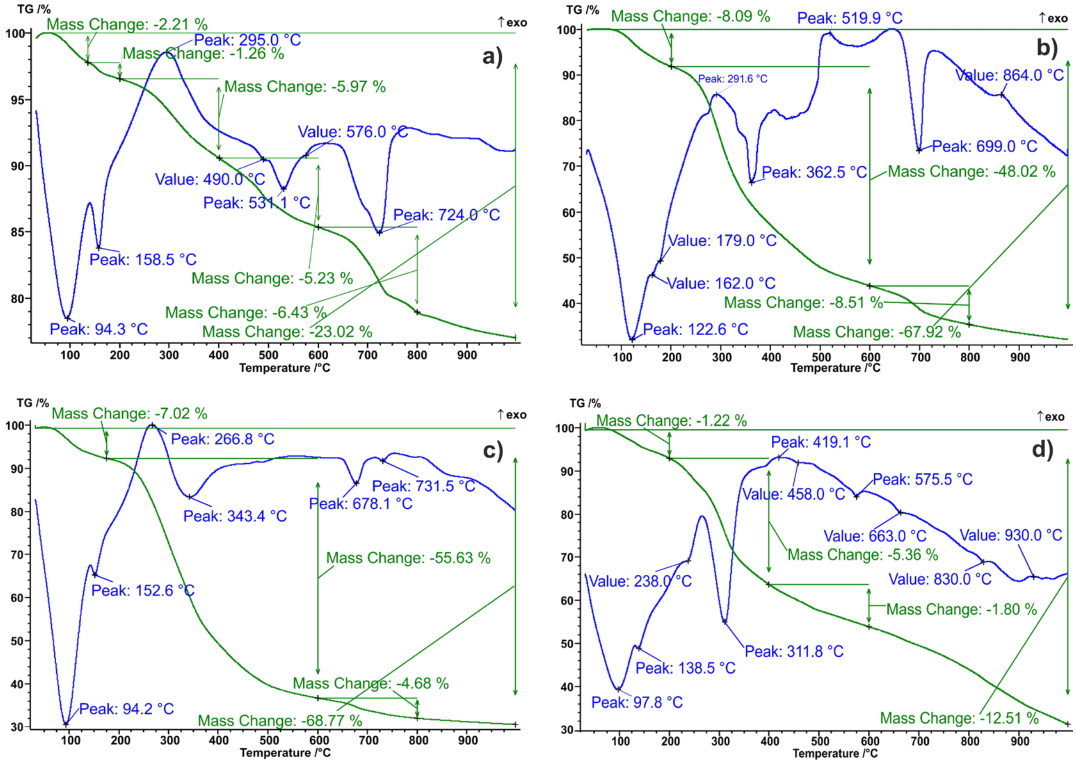

Figure 5. Thermal curves: (**a**) Skeletic Cryosol (Thixotropic) (sample 151); (**b**) Stagnic Cryosol Reductaquic (sample 984); (**c**) *Humic Fluvisol* (sample 1663); (**d**) siltstone (sample KM-6-21).

4. Discussion

For the formation of oxalates, environmental conditions play a significant role, which primarily depend on climate and soils. Among the soil conditions, high humidity, pH, and the presence of calcium-containing minerals are distinguished [55–58]. The studied territory is characterized by a sharply continental cryoarid climate, which negatively affects the vital activity of plants and microorganisms, particularly in determining their growth characteristics [59]. However, the biochemical transformation of various organic compounds during the life cycle is rather evident. Soil parameters mostly determine the reserves of resources for biota.

The moisture necessary for cryomorphic soils is ensured by seasonal thawing of the permafrost, the knob-and-basin or polygonally jointed microrelief of the studied areas, as well as periodic flooding of nearby rivers. The first two samples were selected on the territory in which the knob-and-basin microrelief is almost ubiquitous. The soils in which oxalates are detected occupy the bottom of the depressions; therefore, they develop in conditions of high hydromorphism. They are also characterized by a relatively high content of coarse organic matter. The third sample was taken on the surface of alluvial soil located a few meters from the water level of the Markha River. The river's nourishment is primarily snow and rain. The role of underground nourishment is small; spring and summer–autumn floods are observed, occurring 3–4 times during the warm season, hence Humic Fluvisol soils are characterized by the high moisture content of soil organogenic material. The fourth sample was located on a coastal outcrop that is also exposed to quite extensive river overflow in the warm season. The presence of carbonates also provides for the formation of oxalates. The parent rock of Cryosols is composed of carbonate rocks; alluvial soil contains a small amount of dolomite and montmorillonite, which provides a slightly alkaline and slightly acidic acid–alkali medium on the surface of the sites. Although the presence of carbonates was not detected during the X-ray phase analysis of the siltstone rock, the studied outcrop in general has carbonate veinlets. Thus, in all the above samples, the mineral composition, high humidity, and neutral or slightly alkaline pH of the soil solution predetermined the formation conditions for calcium oxalates. Nevertheless, we note only isolated findings of calcium oxalates, rather than their widespread distribution. Consequently, there must be another requirement that would contribute to the occurrence of calcium oxalates.

All samples were taken within the preserved soils on the technogenically transformed landscapes. Weddellite and whewellite were found on the territory of the Daldyn kimberlite field at the boundary of the organic horizon and moss-lichen cushion in the industrial site of the mining and processing plant. Sample 984 was found on the territory located between the slurry pipeline of highly mineralized water disposal in a natural permafrost reservoir and a complex designed for the storage or disposal of waste from kimberlites [60]. Therein the largest amount of coating consisting of weddellite was found. It should be noted that dead lichens were found in the areas with coating. Sample 151 was found far beyond the disposal of drainage waters, man-made landfills, and tailing dumps. Nevertheless, in relation to the extraction of diamonds, the studied territory has been developed for a prolonged period of time, thus the influence of man-made impacts is observed throughout the area. For example, the landfills of underground brine disposal and penetration of drainage water to them act as an additional strain on the ecosystem. It is possible that an underground landfill and a tailings dump could indirectly affect the state of the vegetation of the territory and contribute to the formation of oxalate, since highly mineralized waters possess a calcium chloride composition; their release could trigger excessive accumulation of calcium in lichens. Results of the study of the formation conditions of calcium oxalates on the territory of the Daldyn kimberlite field revealed that calcium oxalates synthesize lichens, therefore demonstrating a protective reaction due to changes in the micro- and macronutrient composition of natural soils [61]. Lichens change the shape of the growth of thalli and accumulation of a high number of oxalates, which also according to [11] occurs during granulation of the thallus; in this case, the podecia covered with granules show a higher capacity for the accumulation of heavy metals.

Sample 1663 was found in the form of a film on the surface of plant residues; according to [62,63], it was probably formed by micromycetes in the process of primitive soil formation of alluvial soil. A distinctive characteristic of the alluvial soils is periodic inundation by thawing waters, which is accompanied by the penetration and deposition of new mineral material on the soil surface as well as the burial of the horizon and formation of a new one, sometimes with a completely different composition. Therefore, it is probably the case that micromycetes have developed a mechanism for the synthesis of calcium oxalate as a way of adapting to the frequently changing composition of the underlying rock. According to the works of [64–66], it was discovered that the biocrystallization of oxalates contributes to the detoxification or mitigation of water, salt, and temperature stresses, providing tissue hardness and mechanical support.

Weddellite on the surface of siltstone is also a product of initial soil formation and is possibly associated with the vital activity of micromycetes; however, its abundant manifestation could also represent an intoxication method. It has been established that an increase in the synthesis of oxalic acid in plants is possible as a form of adaptation mechanism to the environmental conditions, consequent to heavy metal intoxication [9,12,24,67]. The rocks with a coating formed on their surface (sample KM-6-21) are characterized by the presence of arsenic, a major component of gold-bearing ores in the form of arsenopyrite. As is known, under the effects of atmospheric precipitation and humidity from the nearby river, gradual destruction of the rock occurs on the outcrops. At the same time, sulfides and other minerals begin to oxidize, releasing contained iron, sulfur, and arsenic.

It is interesting that in one case, a monohydrate whewellite was formed, while in the other—a dihydrate. Oxalates are commonly found in the form of whewellite; significantly less often, weddellite is also recorded [8]. The occurrence of unstable weddellite can be explained by the peculiarities of natural and climate factors. For example, it was previously established that the crystallization of weddellite is aided by low temperatures and high humidity with little exposure to sunlight, as well as an excess of calcium ions in the medium [55–58,67]. These conditions are typical for the knob-and-basin microrelief of the studied territory: moisture accumulates in the depressions, sparse vegetation and dense moss-lichen cover prevents sunlight penetration. Due to the host carbonate rocks of the Daldyn kimberlite field, a high content of calcium ions and optimal redox conditions of the soil environment for the formation of oxalate are observed in the soils. Thus, favorable conditions are established for the formation of weddellite in the depressions of the microrelief.

The soil containing sample 151 was located in the forest, although not in a depression, which is presumably the reason why only monohydrate oxalate was detected there. Similarly, with higher or lower humidity conditions, the formation of whewellite on alluvial soil and weddellite on rock can be explained. The alluvial soil is located a few meters from the Markha River and was the least flooded at the time of sampling, while sample KM-6-21 was located relatively closer to the Allah-Yun River, wherein dense vegetation overlies the outcrop providing shade and serving to preserve moisture.

The samples described above are characterized by different soil genesis, yet they possess similar soil moisture conditions, close pH values, and calcium carbonate content. In addition, a certain degree of impact on soils was observed, which led to an increase relative to the background contents of a wide range of trace elements. In all the cases described, calcium oxalates are recorded in the following form: a salt crust on the surface of the soil formed in the depression, in the form of a film at the boundary of the moss-lichen cover and organic horizon, in the form of a coating on the outcrop at the initial stage of soil formation. Therefore, with a certain probability, it can be assumed that calcium oxalates are soil neoformations that signify special conditions or man-made impact.

The discovery of weddellite and whewellite on the territory of Yakutia (Russia) under conditions of a sharply continental cryoarid climate, permafrost, and taiga vegetation expands the area of oxalate finds and the conditions for their formation.

5. Conclusions

The impact of a sharply continental cryoarid climate on the vital activity of plants and microorganisms in the region is significant; however, the required humidity is provided by seasonal thawing of the permafrost, the microrelief depression of the studied territory, and the proximity of rivers that undergo waterlogging multiple times during the warm period of the year.

We suggest that the detected oxalates have a different genesis, with the first two samples being products of lichen's vital activity, and the third and fourth samples being products of initial soil formation by micromycetes.

We cannot exclude the protective function of oxalates, since the samples were found in the technogenically transformed territory of long-term diamond mining, areas exposed to the industrial waste, and in the oxidized gold-bearing territory composed of siltstones that contain arsenopyrite and pyrite.

Author Contributions: Conceptualization, T.I.V. and Y.B.L.; writing–original draft preparation, T.I.V.; writing—review and editing, Y.B.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Diamond and Precious Metals Geology Institute FUEM-2019-0003 "Evolution of the earth's crust of the North Asian craton, basic-ultrabasic and kimberlite magmatism, diamond content of the Yakutian kimberlite province".

Data Availability Statement: Not applicable.

Acknowledgments: The authors are grateful to N.V. Zayakina and M.V. Kudrin for help and advice.

Conflicts of Interest: The authors declare no conflict of interest.

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