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**Chemical weathering east and west of the emerging
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implications for climate**

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1 Chemical weathering east and west of the emerging Caledonides in the
2 Silurian—early Devonian, with implications for climate

3

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9

10 Abstract

11 The late Llandovery (Silurian)—early Lochkovian (Devonian) climate of
12 the tropical zone is tracked considering orogenesis, global glaciation
13 events and cratonic drift. Mineral and chemical compositions of clay
14 fractions of Canadian (the Franklinian Basin) and Estonian (the
15 Baltoscandian Basin) sedimentary rocks from different sides of the
16 emerging Caledonides were studied, using clay as an index of climatic
17 conditions of the provenance area. Illite is the main clay mineral with
18 addition of orthoclase, muscovite and chlorite in both regions.

19 Authigenic chert is present in some Canadian sections. The similarity of
20 clay minerals and elemental composition in the two regions suggest
21 common chemical weathering conditions. Nevertheless, the Al/Ti ratio of
22 the <1 micron clay fraction, the proxy for climate's aridity–humidity and
23 weathering intensity, reveals differences. The Franklinian Basin in
24 Laurentia shows a shift of climate from humid to semi-humid in pace
25 with the uplift of the Caledonides. The sub-meridional mountain chain in
26 the east reduced the amount of rainfall and, therefore, caused drier
27 climate than could have been expected from the low latitudinal position
28 of the area. The material from the Baltoscandian Basin reveals semi-arid
29 and arid climate for most of the Silurian. Although the southern part of

the Fennoscandian Shield was situated in desert latitudes, the evidence from the provenance of clay suggests that the climate was not fully arid. In Baltoscandia, co-variation between low Al/Ti of clay and negative shifts of $\delta^{13}\text{C}$ of marine carbonates is recorded at some stratigraphical levels suggesting link between humid climatic episodes in mainland and waning of glaciers at the South Pole.

Key words: clay, climate, Al/Ti, Laurentia, Baltica, Silurian

1. Introduction

The Caledonian orogeny affected the climate of Baltica and Laurentia in the Silurian (Fig. 1). Precipitation changed in accordance with the rise of mountain chains. Also, the short-term global events indicated by excursions of carbon isotopes of carbonate (Saltzman 2005; Kaljo et al. 1998) and oxygen isotopes of apatite (Lehnert et al. 2010), were superimposed on regional climatic features. The aim of the present study was to characterize the climate of the equatorial zone west of the emerging Caledonides in Laurentia and the arid tropical zone east of the Caledonides in Baltica. The lithology and mineralogical–chemical composition of clay in the Baltoscandian and Franklinian sedimentary basins were compared. The clay contained characteristic mineral and chemical compositional signatures gained in the process of chemical weathering in the terrestrial provenance. The parent rock may have had a local imprint on the chemical composition of the clay that formed, but these differences were masked by erosional mixing. When climate changed, the compositional differences in clay chemistry changed simultaneously in the same direction, resulting in a new average. The comparison between temporally different averages, preserved in sedimentary record, allows interpretation of alterations in weathering conditions.

59

60 2. Geological background

61 The Franklinian Basin was situated in the northern part of the Laurentia
62 paleocontinent, comprising the northernmost Greenland and extending
63 1,500–2,000 km into the Canadian Arctic Archipelago (Figs. 1; 2). The
64 basin was in the equatorial zone from the Ordovician until the Devonian
65 (Cocks and Torsvik 2011). In the Silurian, it was a shallow-water
66 carbonate basin. The likely provenance of terrigenous sediments was the
67 Canadian Shield consisting of metamorphic and magmatic rocks. Some of
68 the sediment may have come from the problematic land comprising the
69 present-day Ellesmere and other smaller islands (Anfinson et al.
70 2012). The close position of Siberia to the Laurentia and Baltica suggested
71 in the Silurian, was broken off by a new rifting in the Devonian (Golonka
72 2003). The thickness of the Silurian sediments in the Franklinian Basin
73 reached 3–4 km (Thorsteinsson 1958). The first evidence of sediment
74 input from the rising Caledonides occurred at the Ordovician–Silurian
75 boundary in eastern North Greenland. Through the Llandovery an
76 elongate fan system developed parallel to the Franklinian platform margin
77 (Smith and Rasmussen 2008).

78 The Baltoscandian Basin was an epicontinental sea of carbonate
79 accumulation in the southwestern part of the Baltica Plate. The main part
80 of the craton was situated between latitudes 35°S and 10°S in the early
81 Silurian, moving towards the equator with the speed of about 80–100
82 km/Ma and crossing the boundaries of climatic zones (Nikishin et al.
83 1996). Near the Silurian–Devonian transition, the direction of the
84 movement changed (Cocks and Torsvik 2011). The terrigenous
85 components and clay minerals for the Baltoscandian Basin formed on the
86 flat, slightly uplifted Fennoscandian Shield (Fig. 3a). Contemporaneous
87 with the development of the Caledonides the Fennoscandian Shield

smoothly emerged and joined with the Sarmatian Shield (Fig. 1c), causing regression of the Baltoscandian Basin (Kaljo et al. 1977; Baarli et al. 2003; Nikishin et al. 1996). Thickness of the Silurian sediments varied from 200 m in Estonia up to 2–3 km in the deep southwestern part of the Baltoscandian Basin (Verniers et al. 2008). The Pechora Basin of the near-polar Urals was a good landmark for tracking the boundary between desert and the equatorial wet climate. In Pechora the upper Silurian limestones replaced the lower Silurian dolomites and evaporites (Baarli et al. 2003; Nikishin et al. 1996) in accordance with the northward drift of Baltica Plate. In the same interval, the Baltoscandian Basin moved within desert latitudes, from 30°S to 15°S.

3. Material

We characterised chemical weathering through chemical and mineral compositions of clay fractions <1 micron. Our investigation showed that neither Canadian nor Estonian samples were heated or damaged by secondary changes, as they dispersed well in dissolving procedures.

3.1. The Canadian material

The rock samples were collected by one of the authors (T. M.) during her expedition to the Canadian Arctic Archipelago in 1994. The samples from the sections of Cornwallis and Baillie Hamilton islands represent transition of deep and shallow facies, where limestones alternate with graptolitic shales (Fig. 2b) (Melchin and Holmden 2006). The stratigraphy of the Canadian samples follows Märss et al. (1998) and Märss and Männik (2013). The Cape Phillips Formation (Fm.) of Baillie Hamilton Island ranges from the upper Telychian through Ludfordian. The formation contains alternations of microlaminated mudstone (graptolitic shale), siltstone and limestone (grainstone, rudstone,

floatstone) layers of 5–30 cm in thickness. The Barlow Inlet Fm. of Cornwallis Island, Read Bay south outcrop, represents the Pridoli Series and consists of limestone, dolomite and shale. The Devonian (Lochkovian) Sophia Lake Fm. and the overlying Snowblind Bay Fm., in the northern section of Read Bay consist of limestone and dolomite with siltstone and sandstone interbeds and conglomerate (Fig. 4).

3.2. The Baltoscandian material

The Baltoscandian material comes from the shallow shelf of Estonia, Latvia and Lithuania (Fig. 3b). The majority of samples, representing the Wenlock, Ludlow and lower Pridoli Series (Kaljo et al. 1998), were collected from the Ohesaare core from the Saaremaa Island, the upper Llandovery (Telychian) samples come from the Kirikuküla and Paatsalu cores from mainland Estonia. The Kolka-54 core from western Latvia and the Taurage core from Lithuania represent the lower part of the Lochkovian. The lithology, mainly limestone, dolomite and marlstone, is shown in a composite section (Fig. 5.) To ensure that the clay comes from a single provenance area, shallow-shelf samples were used. The deep-shelf material from different sources brought into the Baltoscandian Basin by currents (Kiipli et al. 2009) would have made the comparison uncertain and was, therefore, excluded.

4. Methods

The clay fraction was mainly separated from calcareous material. The samples were treated with 1N HCl. For dissolution of 100 g of calcite, 2 litres of acidic solution was needed. The insoluble residue was settled for 24 hours in a 0.1% Na-pyrophosphate solution. The unsettled part, the clay fraction $<1\mu\text{m}$, was centrifuged and then dried. For the Canadian samples, the initial sample weight was about 100 g. The insoluble

146 residue, in the amount of 20%, consisted mainly of clay fraction and
147 sand- and silt-sized quartz grains. The organic carbon content varied from
148 0.5 to 5%, treatment with H_2O_2 was used for these samples.
149 The Estonian samples were more clayey thereby 30–50 g of the initial
150 calcareous material was taken. The insoluble residue consisted of clay
151 and silt without sand and organic matter.
152 The clay fraction was analysed for chemical and mineral composition.
153 Pressed clay pellets were subjected to X-ray fluorescence (XRF) analysis
154 using the Bruker AXS S-4 spectrometer at the Institute of Geology at
155 TUT. The detection limit for the main elements heavier than P was
156 0.01%, for lighter elements, 0.1%. The chemical analyses used in Figs 4
157 and 5 are given as calculated averages of the global series in Table 1. The
158 mineral composition of the clay fraction was analysed by X-ray
159 diffractometry (XRD).
160 As a proxy for climate and intensity of chemical weathering, the
161 $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio of clay fraction was used. Al and Ti are bound together
162 in clay-forming process and the characteristic Al/Ti ratio is preserved in
163 sedimentary basins (Ronov and Migdisov 1965). Al and Ti are immobile
164 elements in near-neutral conditions, but their migration diverges
165 according to the pH of the environment. Al goes into the solution at pH
166 <4 and pH >10 , whereas Ti is mobile at pH <2 . In clays, Ti can replace
167 Al in the crystal lattice depending on the intensity of chemical
168 weathering. Temperature and precipitation determine the intensity of
169 chemical weathering which is stronger in the humid and weaker in the
170 arid climate (van de Kamp 2010). Investigating different geological
171 sections, Akul'shina (1976) elaborated the empirical relationship for the
172 $\text{Al}_2\text{O}_3/\text{TiO}_2$ (here referred to as Al/Ti) ratio and climate: Al/Ti <20
173 indicates humid climate and intense chemical weathering; the ratio >30
174 points to arid climate and weak chemical weathering. Semi-humid and

175 semi-arid conditions stay between the values of 20 and 30. The Al/Ti of
176 the clay fraction separated from carbonate rocks of the Baltoscandian
177 Basin has previously been applied in differentiating humid and arid
178 climates of the Upper Ordovician and Silurian in the Fennoscandian
179 Shield (Kiipli et al. 2012).

180

181 5. Results

182 5.1. Clay fraction of Franklinian Basin

183 The main clay mineral of the clay fraction is illite. Few Telychian
184 samples reveal traces of kaolinite. Clay mineral content depended on
185 authigenic chert (Thorsteinsson 1958) from Baillie Hamilton and northern
186 Cornwallis islands. From Llandovery to Ludlow, the amount of quartz
187 (mainly chert) reaches 74% in the fraction $<1\ \mu\text{m}$. In the Přidoli chert is
188 lacking and only 2% of terrigenous quartz was detected in the Read Bay
189 sections (Fig. 4). To eliminate the silica influence, the Al-normalisation
190 of element contents was used. The $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio in clay stays rather
191 constantly around 0.33. A shift towards lower values occurs in the
192 Devonian, as the MgO content increases. The rise in MgO starts in Přidoli
193 time and is associated with the rising chlorite content of up to 2–3%. In
194 the lower Devonian, the MgO reaches 10.6% and magnesian chlorite-
195 smectite, corrensite, is detected in addition to chlorite. Dispersed
196 orthoclase is present in the clay fraction, its content reaching 5–6% in the
197 upper Přidoli and Lochkovian. The content of muscovite polytype 2M_1 is
198 around 10% in the chert-free upper interval. The Al/Ti ratio increases
199 upwards, from 12 in the Telychian up to 25 in the Přidoli. The trend is
200 interrupted by random higher and lower values.

201

202 5.2. Clay fraction of the Baltoscandian Basin

203 The clay fraction of the Baltoscandian Basin (Fig. 5) consists of illite,
204 muscovite 2M₁, minor chlorite, quartz and orthoclase—very similar to the
205 Canadian clay, excluding the component of authigenic chert in the
206 Canadian material. Authigenic hematite adds red hue to the Devonian
207 section, whereas the Silurian rocks are grey. The chemical composition of
208 the clay fraction is rather uniform through the Silurian, shown by Al-
209 normalised elements (Fig. 5). Some fluctuations occur in the lower
210 Telychian and in the upper Wenlock. The Al/Ti ratio is between 25 and
211 30 during most of the Silurian and in the Lower Devonian. In the lower
212 Telychian Rumba Fm. the Al/Ti ratio below 20 is recorded in the
213 Estonian Kirikuküla and Paatsalu cores (Fig. 6).

214

215 6. Discussion

216 6.1. Climate at the equator west of the Caledonides

217 Oceanic illite, chlorite and kaolinite are generally related to latitude
218 (Fütterer 2000). In the Franklinian Basin, the main Silurian clay mineral
219 is illite. Kaolinite, characteristic of equatorial humid climate, is absent,
220 though the weathering provenance was situated near the equator. In the
221 Telychian, before the main orogeny, low Al/Ti ratio indicates humidity,
222 but the lack of kaolinite (traces, found in Telychian samples) shows that
223 the humidity was only moderate. In accordance with the uplift of the
224 Caledonides, the clay fraction gained more non-weathered mineral
225 particles pointing to the increasing influence of the mountains. Also, the
226 rising Al/Ti ratio shows weakening of chemical weathering and
227 movement towards semi-humid and semi-arid climates from
228 Sheinwoodian up to the end-Silurian (Fig. 4). Very likely, the rising sub-
229 meridional mountain ranges hindered the reach of moist trade winds to
230 the Canadian Shield (Fig. 1b, c).

231 6.2. Climate in the tropics east of the Caledonides

232 In Baltoscandia, starting from the Telychian, silt and sand fractions
233 gained more muscovite (Viiding et al. 1983). Also, in the clay fraction,
234 the content of orthoclase and muscovite $2M_1$ increased, pointing to the
235 rising influence of the Caledonides from the middle Wenlock on (Fig. 5).
236 Al/Ti shows semi-arid/arid climate. The Baltica's drift sets the southern
237 Fennoscandian Shield at the desert latitudes (Fig. 1). The lithology of the
238 Pechora Basin in the northern side of the Baltica Plate helps to refine the
239 positions. In the Llandovery, preceding the Caledonian Orogeny, the
240 Baltoscandian sections consisted of lime- and marlstone, the Pechora
241 Basin of dolomites and evaporites (Nikishin et al. 1996). The Pechora
242 area was situated around 15°S and the Baltoscandian Basin about 1,500
243 km southwards, near 30°S (Fig. 1a). In the Wenlock (Fig. 1b), the
244 replacement of evaporites and dolomites by limestones–marlstones
245 (Baarli et al. 2003) indicates the reach of Pechora to the equatorial humid
246 belt. At the same time, the dolomite and occurrences of gypsum in the
247 Podolia, Ukraine, (Tsegelnyuk and Bukatchuk 1974) show advance of
248 tropical desert in Baltoscandia (Fig. 1b,c). In the latest Silurian, the
249 southern part of the Fennoscandian Shield together with the adjacent
250 Baltoscandian Basin may have approached, but not entered, the equatorial
251 zone, indicated by replacement of dolomite by limestones–marlstones of
252 the latest Silurian (Kaljo et al. 1970). Also, the decline in Al/Ti ratio of
253 the latest Pridoli suggests semi-humid conditions (Fig. 5). The semi-
254 arid/arid climate of the Fennoscandian desert, not achieving strongly arid
255 conditions, indicates presence of modest rainfalls. South-east winds from
256 southern seas regulated the moist regime in Fennoscandia, similar to
257 monsoons in present-day India.

258

259 6.3. Devonian changes

260 In the early Devonian, the erosion of the Caledonides prevailed bringing
261 about changes in chemical and physical weathering in Baltica and
262 Canada. Mg-corrensite in the Lochkovian (lowermost Devonian) clay
263 suggests new environmental conditions of clay formation in Canada.
264 Occurrence of saline lagoons (Drits and Kossovskaya 1990) or
265 intramontane shallow water bodies, similar to those of western Norway in
266 the Devonian (Fossen et al. 2008), may be possible. In Baltoscandia, the
267 Ordovician–Silurian carbonate basin was replaced by siliciclastic
268 dominated setting. In Estonia, kaolinite appears in the Pragian (Kemer
269 Regional Stage) (Viiding et al. 1983), indicating an equatorial location of
270 clay provenance.

271

272 6.4. Short-term global climatic events

273 During the Silurian the global climate was affected by several cooling
274 events reflected by positive excursions of $\delta^{13}\text{C}$ pointing to south polar
275 glaciations (Saltzman 2005). In contrast, the negative excursions may
276 correspond to retreat of ice-sheets. In Baltoscandia a co-variation between
277 low Al/Ti of clay and the negative shift of $\delta^{13}\text{C}$ of marine carbonates is
278 recorded in the lower Telychian (Fig. 6). Humidity of the early Telychian
279 (*turriculatus* graptolite zone) was probably caused by a global climatic
280 warming episode (Kiipli et al. 2012). Other co-variations between
281 negative excursions of Al/Ti and $\delta^{13}\text{C}$ occur in the lower Homerian
282 (*lundgreni* graptolite zone) and Gorstian (*nilssoni* graptolite zone).
283 Compared to the lower Telychian, the latter two shifts of Al/Ti are less
284 pronounced. In Canada, there is no co-variation between $\delta^{13}\text{C}$ and Al/Ti,
285 comparing the Al/Ti with isotope data published by Märss et al. (1998).
286 Probably, the influence of the Caledonides overshadows the possible
287 changes in clay composition related to short-term global climatic events.

288

289 7. Conclusions

290 Clay fractions in Silurian carbonates of the equatorial Franklinian and
291 desert-to-subequatorial Baltoscandian basins were similar in composition,
292 and lacked kaolinite. The Al-normalised K_2O , MgO and Fe_2O_3 values
293 were comparable in both areas. Still, the Al/Ti ratio helps to refine
294 climatic differences in time and space. In Baltoscandia in the early
295 Telychian and Laurentia in the upper Telychian and Sheinwoodian,
296 regional climate was more humid than in later times. In Baltoscandia
297 Telychian continental humidity appears to have been due to a short-term
298 global climatic warming event. In the Franklinian Basin that weathering
299 event was overprinted by equatorial humidity. From Wenlock time, both
300 basins show increasing aridity and reduced chemical weathering. In the
301 Franklinian Basin the climate became semi-humid, while the
302 Baltoscandia—south Fennoscandia was arid to semi-arid. The high
303 Caledonian Mountain chain that separated the two areas, in addition to
304 latitude, controlled precipitation and regional climates.

305

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314

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316 References

- 317 Akul'shina, E.P. 1976. Methods for determining weathering conditions,
318 sedimentation and post-sedimentary transformations according to
319 clay minerals. *In* Clay minerals as indicators of rock forming
320 conditions. *Edited by* E.P. Akul'shina. Nauka, Novosibirsk, pp. 9–
321 37 (in Russian).
- 322 Anfinson, O.A., Leier, A.L., Gaschnig, R., Embry, A.F., and Dewing, K.
323 2012. U–Pb and Hf isotopic data from Franklinian Basin strata:
324 insights into the nature of Crockerland and the timing of accretion,
325 Canadian Arctic Islands. *Canadian Journal of Earth Science*, **49**:
326 1316–1328.
- 327 Baarli, B.G., Johnson, M.E., and Antoshkina, A.I. 2003. Silurian
328 stratigraphy and paleogeography of Baltica. *In* Silurian lands and
329 seas. *Edited by* E. Landing and M.E. Johnson. New York State
330 Museum Bulletin, **493**: pp. 3–34.
- 331 Cocks, L.R.M., and Torsvik, T.H. 2011. The Palaeozoic geography of
332 Laurentia and western Laurussia: A stable craton with mobile
333 margins. *Earth-Science Reviews*, **106**: 1–51.
- 334 Drita, V.A., and Kossowskaya, A.G. 1990. Clay minerals: smectites,
335 mixed-layer silicates. Nauka, Moscow, pp. 214 (in Russian).
- 336 Fossen, H., Dallmann, W., and Andersen, T.B. 2008. The mountain chain
337 rebounds and founders. *In* The making of a land—Geology of
338 Norway. *Edited by* I.B. Ramberg, I. Bryhni, A. Nøttvedt, and K.
339 Rangnes. Norsk Geologisk Forening, Trondheim, pp. 232–259.
- 340 Fütterer, D.K. 2000. The solid phase. of marine sediments. *In* Marine
341 geochemistry. *Edited by* H.D. Schulz and M. Zabel. Springer-
342 Verlag Berlin Heidelberg, pp.1–22.
- 343 Golonka, J., Bocharova, N.Y., Ford, D., Edrich, M.E. Bednarczyk, J., and
344 Wildharber, J. 2003. Paleogeographic reconstructions and basins

- development of the Arctic. *Marine and Petroleum Geology*, **20**:
211–248.
- Kaljo, D., and Jürgenson, E. 1977. Sedimentary facies of the East Baltic
Silurian. *In* *Facies and fauna of the Baltic Silurian. Edited by D.*
Kaljo. Academy of Sciences of the Estonian SSR, Institute of
Geology, Tallinn, pp. 122–148 (in Russian with English abstract).
- Kaljo, D., and Martma, T. 2000. Carbon isotopic composition of
Llandovery rocks (East Baltic Silurian) with environmental
interpretation. *Proceedings of the Estonian Academy of Sciences*
Geology, **49**: 267–283.
- Kaljo, D., Kiipli, T., and Martma, T. 1998. Correlation of carbon isotope
events and environmental cyclicity in the East Baltic Silurian. *New*
York State Museum Bulletin, **491**: 297–312.
- Kaljo, D., Klamann, E., Nestor, H., Einasto, R., and Jürgenson, E. 1970.
Facies and evolution of the basin. *In* *Silur Estonii. Edited by D.*
Kaljo. Valgus, Tallinn, pp. 301–317 (in Russian with English
abstract).
- Kiipli, E., Kiipli, T., and Kallaste, T. 2009. Reconstruction of currents in
the Mid-Ordovician–Early Silurian central Baltic Basin using
geochemical and mineralogical indicators. *Geology*, **37**: 271–274.
- Kiipli, E., Kiipli, T., Kallaste, T., and Siir, S. 2012. $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio of
the clay fraction of Late Ordovician–Silurian carbonate rocks as an
indicator of palaeoclimate of the Fennoscandian Shield.
Palaeogeography, Palaeoclimatology, Palaeoecology, **365–366**:
312–320.
- Kiipli, T., Kallaste, T., and Nestor, V. 2010a. Composition and
correlation of volcanic ash beds of Silurian age from the eastern
Baltic. *Geological Magazine*, **147**: 895–909.

- 373 Kiipli, T., Kallaste, T., Nestor, V., and Loydell, D.K. 2010b. Integrated
374 Telychian (Silurian) K-bentonite chemostratigraphy and
375 biostratigraphy in Estonia and Latvia. *Lethaia*, **43**: 32–44.
- 376 Kiipli, T., Einasto, R., Kallaste, T., Nestor, V., Perens, H., and Siir, S.
377 2011. Geochemistry and correlation of volcanic ash beds from the
378 Rootsiküla Stage (Wenlock—Ludlow) in the eastern Baltic.
379 *Estonian Journal of Earth Sciences*, **60**: 207–219.
- 380 Lehnert, O., Männik, P., Joachimski, M.M., Calner, M., and Frýda, J.
381 2010. Palaeoclimate perturbations before the Sheinwoodian
382 glaciation: A trigger for extinctions during the ‘Ireviken Event’.
383 *Palaeogeography, Palaeoclimatology, Palaeoecology*, **296**: 320–
384 331.
- 385 Loydell, D.K. 2012. Graptolite biozone correlation charts. *Geological*
386 *Magazine*, **149**: 124–132.
- 387 Märss, T., and Männik, P. 2013. Revision of Silurian vertebrate biozones
388 and their correlation with the conodont succession. *Estonian*
389 *Journal of Earth Sciences*, **62**: 181–204.
- 390 Märss, T., Caldwell, M., Gagnier, P., Goujet, D., Männik, P., Martma, T.,
391 and Wilson, M. 1998. Distribution of Silurian and Lower Devonian
392 vertebrate microremains and conodonts in the Baillie-Hamilton and
393 Cornwallis island sections, Canadian Arctic. *Proceeding of the*
394 *Estonian Academy of Sciences Geology*, **47**: 51–76.
- 395 Melchin, M.J., and Holmden, C. 2006. Carbon isotope chemostratigraphy
396 of the Llandovery in Arctic Canada: Implications for global
397 correlation and sea-level change. *GFF*, **128**: 173–180.
- 398 Nikishin, A.M., Ziegler, P.A., Stephenson, R.A., Cloething, S.A.P.L.,
399 Furne, A.V., Fokin, P.A., Ershov, A.V., Bolotov, S.N., Korotaev,
400 M.V., Alekseev, A.S., Gorbachev, V.I., Shipilov, E.V., Lankreijer,
401 A., Bembinova, E.Yu., and Shalimov, I.V. 1996. Late Precambrian

- 402 to Triassic history of the East European Craton: dynamics of
403 sedimentary basin evolution. *Tectonophysics*, **268**: 23–63.
- 404 Ronov, A.B., and Migdisov, A.A. 1965. Main features of the
405 geochemistry of elements-hydrolysates in processes of weathering
406 and sedimentation. *Geochimiya*, **2**: 131–157 (in Russian).
- 407 Saltzman, M.R. 2005. Phosphorus, nitrogen, and the redox evolution of
408 the Paleozoic oceans. *Geology*, **33**: 573–576.
- 409 Smith, M.P., and Rasmussen, J.A. 2008. Cambrian-Silurian development
410 of the Laurentian margin of the Iapetus Ocean in Greenland and
411 related areas. *In* The Greenland Caledonides: evolution of the
412 northeast margin of Laurentia. *Edited by* A.K. Higgins, J.A. Gilotti,
413 and M.P. Smith. The Geological Society of America Memoir, **202**:
414 Boulder, Colorado, USA, pp. 137–167.
- 415 Thorsteinsson, R. 1958. Cornwallis and Little Cornwallis islands district
416 of Franklin Northwest territories. Geological Survey of Canada
417 Memoir, **294**: pp. 134.
- 418 Tsegelnyuk, P.D., and Bukatchuk, P.D. 1974. The SW slope of the
419 Ukrainian Shield. *In* Stratigraphy of the USSR v. IV, part 1. *Edited*
420 *by* D.E. Aisenverg. Naukova Dumka, Kiev, pp. 156–173 (in
421 Ukrainian).
- 422 Van de Kamp, P. 2010. Arkose, subarkose, quartz sand, and associated
423 muds derived from felsic plutonic rocks in glacial to tropical humid
424 climates. *Journal of Sedimentary Research*, **80**: 895–918.
- 425 Verniers, J., Maletz, J., Kříž, J., Žigaite, Ž., Paris, F., Schönlaub, H.P.,
426 and Wrona, R. 2008. Silurian. *In* The geology of Central Europe,
427 Volume 1: Precambrian and Palaeozoic. *Edited by* T. McCann.
428 Geological Society London, pp. 249–302.
- 429 Viiding, H.A., Kleesment, A.E., Konsa, M., Heinsalu, H., and Jürgenson,
430 E. 1983. Evolution of the terrigenous component of sedimentary

rocks of the southern slope of the Baltic Shield. *In* Terrigenous minerals of the Baltic sedimentary rocks. *Edited by* H.A. Viiding. Academy of Sciences of Estonia, Tallinn, pp. 7–22 (in Russian).

Tables

Table 1. Average values, in wt%, of main chemical elements of the clay fraction.

Figures

Fig. 1. Silurian palaeogeography around the colliding continents.

Positions of Baltica, Laurentia and Siberia in Llandovery (a), Wenlock (b) and latest Silurian (c) are composed using data from Cocks and Torsvik (2011) and Golonka et al. (2003). Lithologic data are included from Baarli et al. (2003), Nikishin et al. (1996), Tsegelnyuk and Bukatchuk (1974), Cocks and Torsvik (2011), Golonka et al. (2003). Wind directions are proposed by analogy with present day world.

Fig. 2. Location map of Arctic Canada with star marking the study area (a); sampling points in the Cornwallis and Baillie Hamilton islands of the Canadian Arctic Archipelago, the facies after Melchin and Holmden (2006) (b).

Fig. 3. Location map with late Silurian palaeogeographic setting of the Baltoscandia, facies compiled after Baarli et al. (2003) and Kaljo and Jürgenson (1977) (a); sampling points (b).

459 Fig. 4. Franklinian Basin. Stratigraphy (from Märss et al. 1998), selected
460 Al-normalized ratios of main elements, and minerals (in %) of the
461 clay fraction of the composite outcrop section of the Baillie
462 Hamilton and Cornwallis islands.

463
464 Fig. 5. Baltoscandian Basin. Stratigraphy, selected Al-normalized ratios
465 of main elements, and minerals (in %) of the clay fraction of the
466 composite core section of Estonia–Latvia–Lithuania. Depths of
467 global stage boundaries (in m) for the Ohesaare core – from Kaljo
468 et al. (1998); depths of formations of the Kirikuküla core – from
469 Kaljo and Martma (2000).

470
471 Fig. 6. The $\text{Al}_2\text{O}_3/\text{TiO}_2$ of terrigenous clay fraction vs. $\delta^{13}\text{C}$ of marine
472 carbonate of the Estonian composite section of the Baltoscandian
473 Basin. The grey ribbons show intervals of co-variation of negative
474 excursions of Al/Ti and $\delta^{13}\text{C}$. The isotopes of the Ohesaare core
475 from Jaani to Kaugatuma stages from Kaljo et al. (1998); of the
476 Ohesaare cliff, Ohesaare Stage – from Kaljo et al. (2012); of the
477 Kirikuküla core, Late Llandovery – from Kaljo and Martma
478 (2000). Depths and stage boundaries, in meters, of the Ohesaare
479 core, – from Kiipli et al. (2010a; 2010b; 2011). Abbreviations:
480 regional stages—Tž, Tilže; OH, Ohesaare; KG, Kaugatuma; KR,
481 Kuressaare; PD, Paadla; RT, Rootsiküla; JG, Jaagarahu; JN, Jaani;
482 AD, Adavere; global stages—Ludf., Ludfordian; Gorst., Gorstian.
483 Formations (Fm.) in *italic*. Names of graptolite biozones after
484 Loydell (2012).

Fig. 1. Silurian palaeogeography around the colliding continents. Positions of Baltica, Laurentia and Siberia in Llandovery (a), Wenlock (b) and latest Silurian (c) are composed using data from Cocks and Torsvik (2011) and Golonka et al. (2003). Lithologic data are included from Baarli et al. (2003), Nikishin et al. (1996), Tsegelnyuk and Bukatchuk (1974), Cocks and Torsvik (2011), Golonka et al. (2003). Wind directions are proposed by analogy with present day world.

74x36mm (300 x 300 DPI)

Fig. 2. Location map of Arctic Canada with star marking the study area (a); sampling points in the Cornwallis and Baillie Hamilton islands of the Canadian Arctic Archipelago, the facies after Melchin and Holmden (2006) (b).
81x43mm (300 x 300 DPI)

Fig. 3. Location map with late Silurian palaeogeographic setting of the Baltoscandia, facies compiled after Baarli et al. (2003) and Kaljo and Jürgenson (1977) (a); sampling points (b).
72x44mm (300 x 300 DPI)

Fig. 4. Franklinian Basin. Stratigraphy (from Märss et al. 1998), selected Al-normalized ratios of main elements, and minerals (in %) of the clay fraction of the composite outcrop section of the Baillie Hamilton and Cornwallis islands.
86x41mm (300 x 300 DPI)

Fig. 5. Baltoscandian Basin. Stratigraphy, selected Al-normalized ratios of main elements, and minerals (in %) of the clay fraction of the composite core section of Estonia–Latvia–Lithuania. Depths of global stage boundaries (in m) for the Ohesaare core – from Kaljo et al. (1998); depths of formations of the Kirikuküla core – from Kaljo and Martma (2000).

77x32mm (300 x 300 DPI)

Fig. 6

Fig. 6. The $\text{Al}_2\text{O}_3/\text{TiO}_2$ of terrigenous clay fraction vs. $\delta^{13}\text{C}$ of marine carbonate of the Estonian composite section of the Baltoscandian Basin. The grey ribbons show intervals of co-variation of negative excursions of Al/Ti and $\delta^{13}\text{C}$ (see text for explanations). The isotopes of the Ohesaare core from Jaani to Kaugatuma stages from Kaljo et al. (1998); of the Ohesaare cliff, Ohesaare Stage – from Kaljo et al. (2012); of the Kirikuküla core, Late Llandovery – from Kaljo and Martma (2000). Depths and stage boundaries, in meters, of the Ohesaare core, – from Kiipli et al. (2010a; 2010b; 2011). Abbreviations: regional stages—Tž, Tilže; OH, Ohesaare; KG, Kaugatuma; KR, Kuressaare; PD, Paadla; RT, Rootsiküla; JG, Jaagarahu; JN, Jaani; AD, Adavere; global stages—Ludf., Ludfordian; Gorst., Gorstian. Formations (Fm.) in *italic*. Names of graptolite biozones after Loydell (2012).

Table 1. Average values, in wt%, of main chemical elements of the clay fraction

	n	H ₂ O	SiO ₂	Al ₂ O ₃	K ₂ O	Fe ₂ O ₃	MgO	CaO	TiO ₂	MnO	S	*Na ₂ O	*P ₂ O ₅	*Cl
Baltoscandian Basin														
Lochkov	3	8.5	48.7	20.3	6.6	9.6	3.9	0.6	0.76	0.04	0.01	0.2	0.3	0.3
Pridoli	9	9.2	49.1	20.7	7.0	6.9	4.5	0.1	0.74	0.03	0.14	0.2	0.7	0.2
Ludlow	5	10.2	47.9	21.6	7.0	6.1	4.2	0.2	0.74	0.03	0.25	0.2	0.5	0.2
Wenlock	18	9.7	49.3	21.8	7.1	5.6	4.1	0.1	0.76	0.03	0.12	0.2	0.4	0.2
u. Telychian, Velise Fm.	8	9.7	49.3	20.8	7.2	6.5	4.5	0.1	0.82	0.03	0.03	0.2	0.4	0.2
l. Telychian, Rumba Fm.	15	9.5	48.4	20.8	7.2	6.0	4.9	0.1	1.18	0.04	0.17	0.3	0.4	0.2
Franklinian Basin														
Lochkov	5	11.3	46.2	17.9	5.5	6.5	9.0	0.3	0.93	0.03	0.16	0.3	0.5	0.2
Pridoli	8	10.5	47.7	20.0	6.5	6.7	5.3	0.2	0.84	0.04	0.21	0.2	0.7	0.1
Ludlow	7	10.0	60.2	15.0	4.8	3.2	2.2	0.3	0.79	0.01	0.77	0.3	0.6	0.2
Wenlock	9	10.7	61.6	13.7	4.3	3.4	1.8	0.1	0.71	0.01	0.72	0.2	0.9	0.1
Telychian	5	10.1	72.1	8.6	2.9	1.5	1.5	0.2	0.55	0.01	0.61	0.2	0.3	0.1

n--number of samples

*--residue of chemicals from the clay separation

Fm., Formation