Chemie der Erde xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Chemie der Erde

journal homepage: www.elsevier.de/chemer

Trace elements indicating humid climatic events in the Ordovician–early Silurian

Enli Kiipli, Tarmo Kiipli*, Toivo Kallaste, Siim Pajusaar

Department of Geology at Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

ARTICLE INFO

Article history:
Received 27 January 2017
Received in revised form 23 May 2017
Accepted 29 May 2017

Keywords:
Ordovician
Silurian
Palaeoclimate
Baltica
Clay
Rb
Zr
Nb
Ti

ABSTRACT

The chemical composition of the clay fraction separated from the carbonate rock of the north-eastern Baltoscandian Basin was analysed and interpreted. Increased contents of Rb, Zr, Nb, Ti and their Al_2O_3-normalised ratios were detected at several stratigraphical levels in the geological sections of the Middle Ordovician–Upper Llandovery. In the weathering areas, Rb, Zr, Nb, Ti and Al are sensitive to moist conditions in the clay-forming process. In the sedimentary basin, the contents of these elements in clay are preserved and allow to infer past climates. Humid events occurred in the Dapingian, Sandbian, early Katian and Hirnantian (Ordovician) and in the Middle and Late Llandovery (Silurian). Juxtaposition with the sea-level curve shows correlation of five humid climate intervals with eustatic transgressions, suggesting global causes for these climatic changes. The warm and humid events, lasting one to two million years, occurred as climaxes between ice ages. An exceptional humid event within the Hirnantian glacial time occurs during mid-Hirnantian transgression, *i.e.* at a time of relative warming, as well.

1. Introduction

The cyclic alternation of sediments in geological sections has inspired geologists to find the reasons and create different models to illustrate the phenomenon. Oscillation of the sea level generating transgressions and regressions explains the variation of layers of either different grain size or lithological-mineralogical composition (Johnson, 2006; Haq and Schutter, 2008). The alternation of limestone–marlstone involves climatic reasons; the model by Jeppsson (1990) and (Aldridge et al., 1993) describes repeated arid–humid conditions and related changes in oxic–anoxic state of the ocean. After intensive studies of isotopes, particularly of $\delta^{13}C$ and $\delta^{18}O$, a hypothesis was proposed that a number of ice ages had occurred in the Palaeozoic (Azmy et al., 1998; Saltzman and Young, 2005; Saltzman, 2005; Kaljo et al., 2003). In the present study we track the climatic changes recorded in the clay fraction and concentrate on the relationship between humid climatic events and high sea-levels. We focus on the distribution of Rb, Zr, Nb, Ti and Al in the Dapingian–Llandovery geological sections, covering the time from 470 to 435 Ma. The sedimentary rock of the East Baltoscandian Basin, which has received the terrigenous clay from the Fennoscandian Shield, is the source material for investigation.

2. Geological background

The Fennoscandian Shield is situated adjacent to the NE Baltoscandian Basin (Fig. 1). Precambrian rocks of the shield represent the average composition of the continental Earth's crust. The parent rock for chemical weathering consists of metamorphosed schists and gneisses, granitic plutons and smaller mafic bodies (Simonen et al., 1997). The Fennoscandian Shield is flat and the sediment reaching the basin fine-grained, consisting of clay and silt. Limestones and marlstones are the lithological types of the shallow shelf, while in the deep shelf more clayey sediments occur. Illite is the main clay mineral in the shallow shelf (Põlma, 1982). Possible precursor minerals to illite, such as vermiculite, have not been detected. During the Ordovician and Silurian, the Baltic Craton drifted from temperate latitudes towards the Equator (Torsvik et al., 1996; Cocks and Torsvik, 2005). Several glaciations at the South Pole took place at that time. Positive excursions of $\delta^{13}C$ and great gaps in sediments of the shallow shelf reflect the glaciations and sea-level drops (Kiipli et al., 2010; Loi et al., 2010). The time between ice ages can be considered as a warmer period with a higher sea level.

3. Geochemical background

3.1. Formation of Rb, Ti, Nb and Zr in clays

During chemical weathering and the following erosion on large areas the source material is homogenised and achieves the aver-

* Corresponding author.
E-mail address: tarmo.kiipli@ttu.ee (T. Kiipli).

http://dx.doi.org/10.1016/j.chemer.2017.05.002
0009-2819/

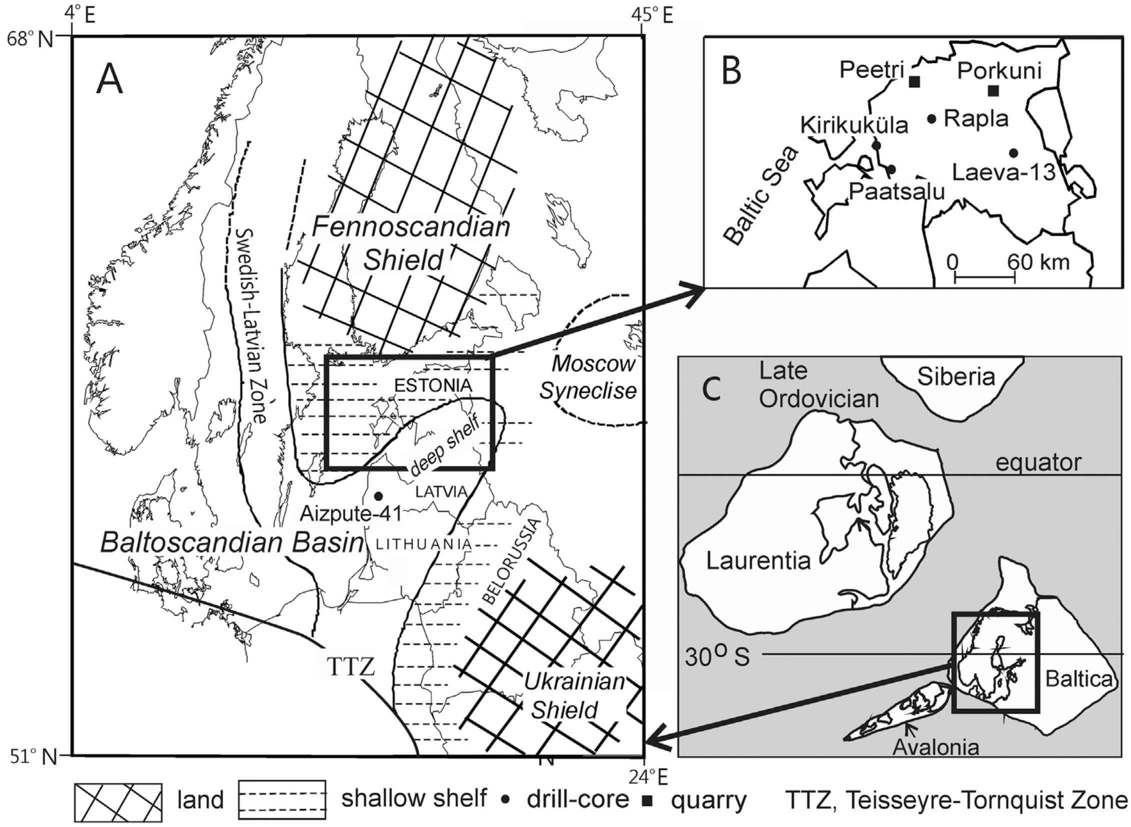

Fig. 1. A sketch-map of the Baltic Palaeozoic Sedimentary Basin (A), sampled cores and quarries in Estonia (B) and Late Ordovician palaeogeography (C) composed according to Cocks and Torsvik (2005), Golonka et al. (2003) and Nikishin et al. (1996).

age chemical composition corresponding to the climate of the particular time. Beside landscape and composition of the parent rock, the temperature and humidity are the most important factors affecting clay composition (Van de Kamp, 2010). In the sedimentary basin, terrigenous clay minerals preserve many signatures obtained during chemical weathering, among others, Al, Rb, Ti, Nb and Zr. The contents of Rb, Ti, Nb, Zr and Al in clay depend on humidity and temperature conditions, as can be inferred from laboratory experiments and recent weathering profiles. Akul'shina (1976), after investigating different geological sections, including the formations with coal interbeds pointing to humid climate, and evaporates assigned to arid climate, elaborated an empirical relationship between Al_2O_3/TiO_2 of clay and climate. The Al_2O_3/TiO_2 ratio below 20 shows humid climate, the ratio over 30—arid, and the values between 20 and 30 refer to semi-humid and semi-arid climates. When using the reciprocal ratio, TiO_2/Al_2O_3, as done in the present study, the value >0.05 points to humid conditions. The increase in the TiO_2/Al_2O_3 ratio of clay at wet climate is explained by higher removal rates of Al from the parent rock at the first stages of chemical weathering. The proportion of Ti increases and Ti is readily incorporated into the new-formed clay, into a tetrahedrally coordinated position (Cornu et al., 1999). Nb and Zr can have similar valence state and an ion radius close to that of Ti, thereby they behave similarly in the clay-forming process. Though Al, Ti, Zr and Nb are generally immobile (Nesbitt et al., 1980; Kiipli et al., 2017), differences in mobility occur; aluminium goes into solution first and Zr is the least mobile of the four (Hodson, 2002). In diagenesis, the mobility of Ti is possible. The anatase found in the clay fraction is very likely related to muscovite or illite and forms in post-depositional processes. Alló (2004) describes the in situ formation of TiO_2 minerals in a non-metamorphised Precambrian sedimentary clay. The TiO_2 minerals have been found in association with the faces (001) of illite flakes or in the pores between flakes, suggesting that Ti originates from clay minerals (Alló, 2004Alló 2004). The co-occurrence of Rb with Ti, Nb and Zr is somewhat unexpected, as Rb^+ is a mobile ion moving easily into solution with Na^+ at the first stages of chemical weathering. Previous studies of Rb, mostly linked to Cs and radiocaesium as radioactive wastes, have shown that Rb and Cs have similarities in sorption into illitic clay (Brouwer et al., 1983). High concentrations of Rb have been recorded in soils of the Savannah River Site, North America. These soils are products of substantial weathering of coastal plain sediments at warm climate and relatively high rainfalls. Elevated Rb contents in these soils have been assigned to hydroxy-interlayered vermiculite (Wampler et al., 2012), a precursor mineral to illite. In Toorongo, east-central Victoria, Australia, the most leached part of the weathering profile also reveals increased Rb contents in residues inherited from the alteration biotite → vermiculite → illite (Nesbitt et al., 1980). Rubidium dissolves readily from the parent rock when the climate turns wet, and adsorbs into the newly-formed clay mineral. Weathered mica particles have suitable sites for Rb^+ fixation in the expanded interlayers of the frayed edges (Zachara et al., 2002; Wampler et al., 2012). The fixation capacity of the frayed edges is regulated by hydroxy-Al polymers (Maes et al., 1999; Meunier, 2007) whose intrusion into crystal structure is sensitive to humidity as well (Nakao et al., 2009a, 2009b).

4. Materials

To ensure that we study comparable material in tracking the climate through the long geological time, the material was collected from Estonian cores of the shallow shelf. Since the deeper part of the Baltoscandian Basin has received sediments from weathering areas of other climate regimes and of different mineral composi-