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Multiply remagnetized Silurian carbonate sequence in Estonia

Ulla Preeden[a], Jüri Plado[a], Satu Mertanen[b], and Väino Puura[c]

[a] Institute of Ecology and Earth Sciences, University of Tartu, Vanemuise 46, 51014 Tartu, Estonia; ulla.preeden@ut.ee
[b] Geological Survey of Finland, Betonimiehenkuja 4, FIN-02151, Espoo, Finland
[c] Institute of Geology, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

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Abstract. Palaeomagnetic studies were carried out on Silurian sedimentary rocks of Estonia. The studied sequence (126 samples from 4 localities) is composed of Silurian lime- and dolostones of Llandovery and Wenlock age (444–423 Ma). Rock magnetic data revealed magnetite, (titano)hematite, and pyrrhotite as the main carriers of remanent magnetization. We found that different secondary magnetizations characterize rocks at different localities, whereas similarities exist between the localities. The virtual poles fall near the Silurian–Early Devonian and Late Palaeozoic segment of the Baltica's APWP. The heritage of these components is related to either syndepositional or early diagenetic changes, and to chemical remagnetization due to late diagenetic processes and/or regional events that affected Baltica during the Late Palaeozoic.

Key words: remagnetization, rock and mineral magnetism, Baltica.

INTRODUCTION

Estonia is located on the southern slope of the Fennoscandian Shield where the Ediacaran to Devonian terrigenous and carbonate sediments cover the ~1.88 Ma Svecofennian crystalline basement. In the Silurian–Early Devonian the area was covered by a shallow cratonic sea where carbonate and fine siliciclastic sediments accumulated (Nestor & Einasto 1997). The Late and post-Palaeozoic deposits are missing in the Estonian geological sequence and, thus, we lack any direct sedimentary evidence for the last 300–400 Ma of the geological history. The absence of Late Phanerozoic rocks suitable for isotope dating makes the palaeomagnetic method the only reliable technique for search of ages of secondary processes previously identified by lithological and mineralogical studies of fracture and pore fillings of the existing sequence (Pichugin et al. 1976; Puura et al. 1996, 1999).

In Palaeozoic carbonates of Europe, the multicomponent remagnetization is a widespread phenomenon (e.g. Nawrocki 1993; Zwing et al. 2002; Zegers et al. 2003; Katinas & Nawrocki 2004). In central Estonia, the Silurian samples from the Rõstla quarry also yielded secondary remagnetizations, pointing to Late Devonian–Mississipian and Cretaceous ages (Plado et al. 2008). In this study, rocks of the Juuru to Jaagarahu Baltoscandian regional stages (Llandovery and Wenlock) were sampled in four quarries of western and central Estonia, in order to find out approximate ages of remagnetizations and to correlate these to geological processes causing post-depositional transformations.

SAMPLING AND LOCALITIES

In 1999–2006 four quarries (Kallasto, Kurevere, Anelema, and Kalana; Fig. 1), representing different stages of Silurian formations in Estonia (Fig. 2), were sampled. Occasionally hand but mostly core samples were taken and oriented by magnetic and/or sun compass. Standard (2.54 cm × 2.54 cm) cylindrical specimens were prepared from the samples.

Llandoverian carbonate rocks were collected from Kallasto (labelled KO) and Kalana (labelled KA) (Fig. 2). The Kallasto outcrop (coastal escarpment) and the abandoned quarry are located about 3.5 km apart in the island of Hiiumaa, NW Estonia. The studied carbonate rocks show highly variable lithological composition. The most characteristic rock types are crinoidal limestones (grainstones) of the Juuru Stage (Nestor 1997; Fig. 2). A total of 25 cylindrical specimens were drilled from four block samples collected in summer 2004 from the Kallasto bank and 61 specimens were obtained from cores of 33 boreholes drilled in the quarry in 2006. In the Kalana quarry cryptocrystalline to argillaceous limestones

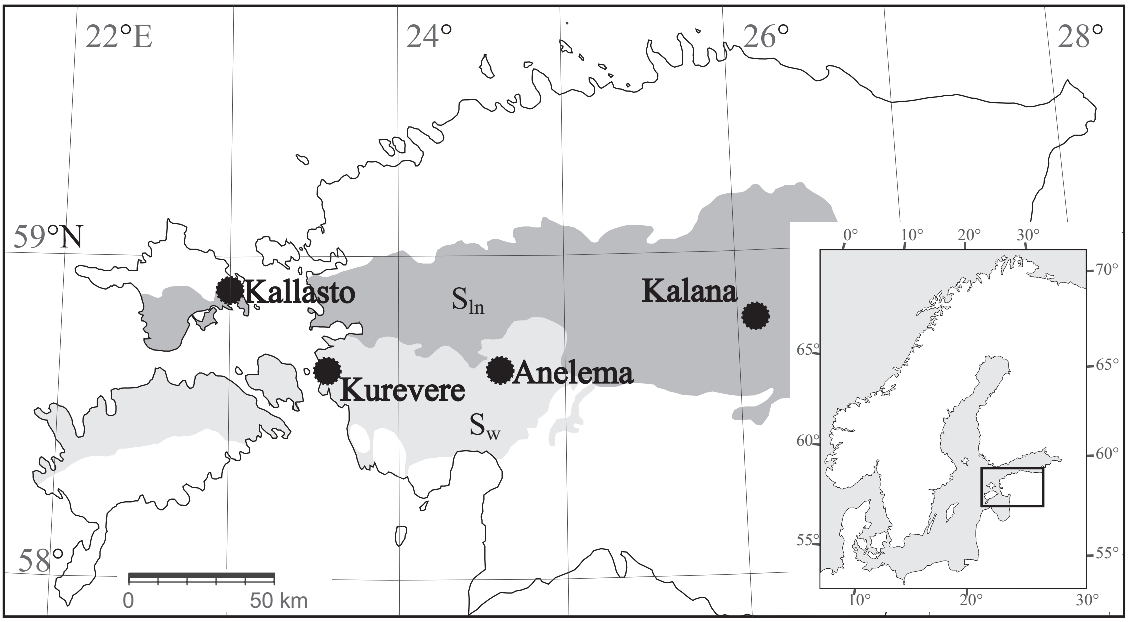

Fig. 1. Sketch map of Estonia. Studied localities are marked with black dots. Dark and light grey shading marks the outcrop areas of the Llandovery (S_{ln}) and Wenlock (S_w) series, respectively.

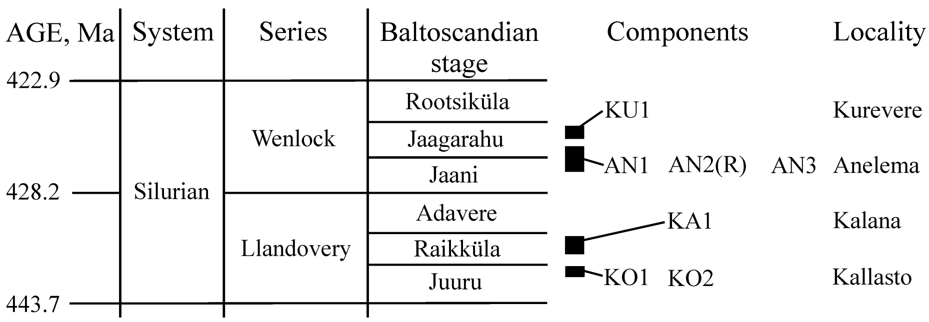

Fig. 2. Stratigraphic scheme of the Silurian system (ages from Gradstein et al. 2004). Black bars show the sampled stratigraphic sections in studied locations and the palaeomagnetic components found. All the components are of normal polarity, except AN2.

with skeletal grainstone lenses and intercalations of the Raikküla Stage (Fig. 2) are exposed. Forty-nine cylindrical specimens were taken from four samples collected in summer 1999 and 76 specimens from 36 boreholes drilled in 2006.

Wenlock rocks are exposed in the Anelema (labelled AN) and Kurevere (labelled KU) quarries (Fig. 2). Dolomitized rocks of the Jaani and Jaagarahu stages are exposed in Anelema. According to the poorly preserved sedimentary structure, the upper part of the section (lower part of the Jaagarahu Stage) consists of fine pellets and is referred to bahamitic type of carbonate sediments. The lower part (Jaani Stage) is argillaceous dolomitized limestone (Einasto 1990). In Anelema 56 specimens were drilled and cut from five block samples collected in summer 2003 and 94 specimens were taken from 34 boreholes drilled during field work in summer 2006. The Kurevere quarry consists of completely dolomitized reef limestone that is surrounded by fine-crystalline bedded dolomite of the Jaagarahu Stage (Fig. 2). Eighty-six specimens were cut from 28 cylindrical cores that were drilled from 10 block samples.

METHODS

Petrophysical and palaeomagnetic measurements were performed at the Paleomagnetic laboratory of the Geological Survey of Finland. Apparent density and magnetic susceptibility were measured before measuring the behaviour of the natural remanent magnetization (NRM). To study the origin of the remanence components, alternating field (AF) demagnetization treatment up to 160 mT in steps between 2.5 and 20 mT was used. After each step, the intensity and direction of the NRM was measured with a superconducting (SQUID) magnetometer. In most cases the demagnetization was stopped earlier, when the intensity of the NRM decreased below the level of instrumental noise (~0.03 mA m^{-1}) or the intensity became unstable. Some specimens were demagnetized thermally but did not yield meaningful results due to mineralogical changes after heating above 300 °C, as indicated by distinct increase in magnetic susceptibility and intensity of the NRM. The results of the demagnetization experiments were plotted in orthogonal projection (Zijderveld 1967) and the components were separated by principal component analysis (Kirschvink 1980). Fisher (1953) statistics was used to calculate mean remanence directions.

Mineralogy of a number of samples was studied in thin sections by optical microscope and X-ray diffractometry (XRD) at the Department of Geology, University of Tartu. Scanning electron microscope and electron microprobe studies were performed at the Institute of Electron Optics, Oulu University. For rock magnetic investigation acquisition of the isothermal remanent magnetization (IRM) and Lowrie (1990) test were performed.

Virtual geomagnetic poles (VGPs) were calculated for each remanence component and plotted on the APW path (Torsvik & Cox 2005) by using the GMAP program of Torsvik and Smethurst (http://www.geophysics.ngu.no).

RESULTS

Mineralogy

Optical microscope was used to evaluate the size, position, and amount of opaque minerals. Two main variations were recognized: (i) opaque minerals disseminated in the carbonate matrix or/and (ii) surrounding the voids. The opaque minerals that fill or surround the voids represent a later generation than the carbonate matrix. Goethite and hematite are the main magnetic minerals according to XRD studies. In addition, a substantial amount of pyrite was detected with electron microprobe studies. In some cases iron oxides replace partly or completely pyrite (Fig. 3), which can be one source for the formation of secondary magnetite that due to oxidation may have eventually altered to hematite.

In order to further identify magnetic carriers, the acquisition of the IRM was studied. During the IRM experiments two types of behaviour were observed (Fig. 4). Specimens from Kallasto and Kurevere (left sides of Fig. 4A and 4D) show a sharp increase in IRM intensity up to 150 mT and a slight but continuous increase at higher fields without reaching saturation at the maximum available field of 1.5 T, thus indicating a mixture of both low (majority) and high coercivity minerals. The specimens from Kalana and Anelema (left sides of Fig. 4B and 4C) are characterized by continuous and gradual increase in IRM intensity up to the maximum applied field, diagnostic for the predominance of high coercivity minerals.

Triaxial IRM demagnetization highlights the unblocking temperatures of the remanence carriers. In Kallasto rocks (right side of Fig. 4A), mineralogical changes of low and high coercivity fractions take place at 300 °C, possibly due to alteration of pyrrhotite, not identified by microscopical studies. The medium coercivity fraction shows also the presence of magnetite (max unblocking temp. 580 °C). In specimens from Kalana and Anelema (right sides of Fig. 4B and 4C, respectively) the first drop in intensity is seen near 100 °C, related to goethite. In the Kalana sample a decrease in intensity in soft and hard fractions is rather abrupt around 620 °C, being related either to magnetite or titanohematite. In Anelema, the soft and hard fractions decrease linearly up to 680 °C, confirming the presence of hematite. In the Anelema specimen the medium fraction is demagnetized around 580 °C, indicating the presence of magnetite. Figure 4D represents Kurevere, where the carriers of magnetization are magnetite (580 °C) and possibly pyrrhotite (~320 °C).

Palaeomagnetic behaviour

Magnetization of carbonate rocks is low with the intensities of the NRM between 0.02 and 0.48 mA m^{-1} and magnetic susceptibilities (volume normalized) between -40×10^{-6} and 54×10^{-6} SI (see Table 1 for mean values). The low values indicate a low content of ferromagnetic minerals, as limestones usually contain only about 0.01% magnetic material (Lowrie 1997). In a study of Estonian Silurian carbonates (Shogenova 1999)

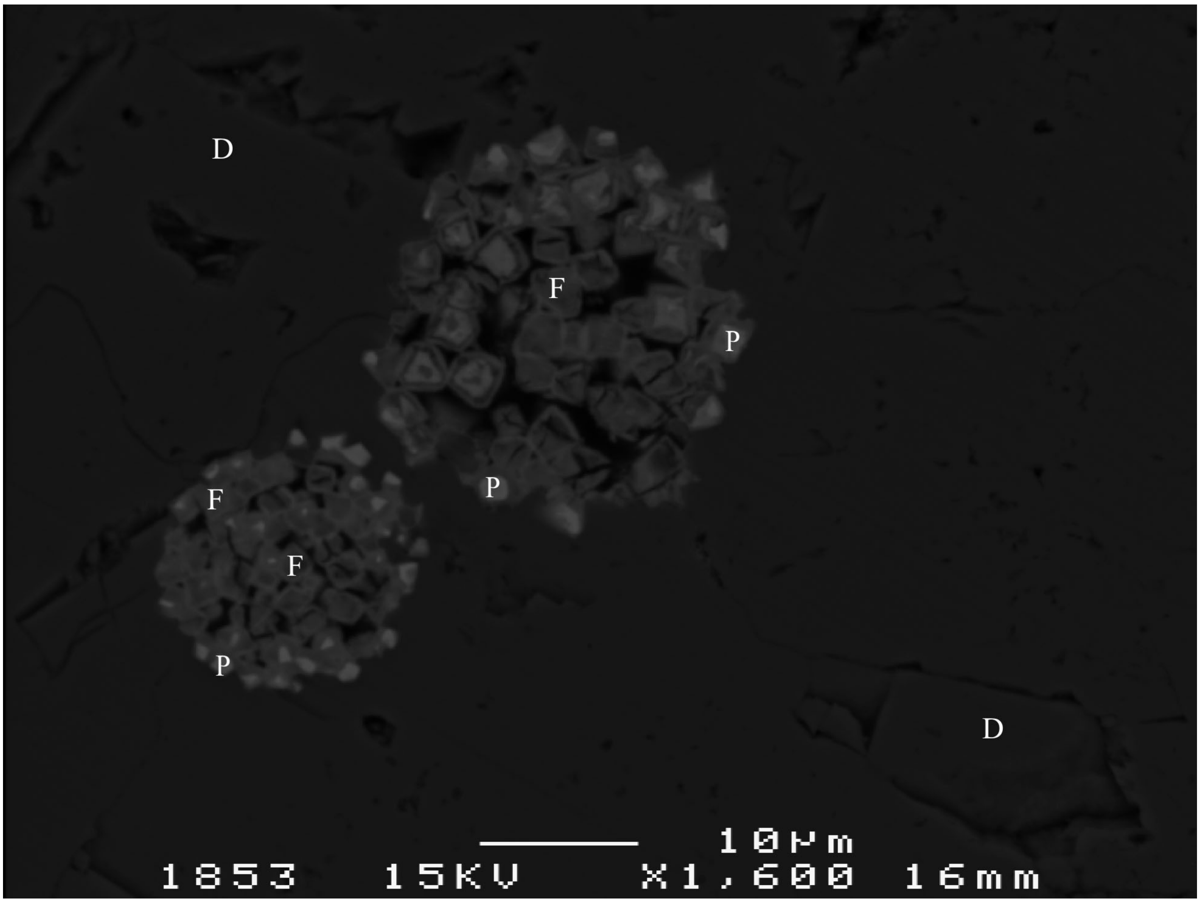

Fig. 3. Backscattered electron image by scanning electron microscope of relict pyrite (P), which has been replaced by iron oxide (F) in thin section of dolomite (D) from Kurevere (sample AB7).

the average content of total iron oxides is about 0.3% in limestones and about 0.6% in dolomites. Even if the NRM intensities and susceptibility values are low, stable remanence components can still be determined.

In **Kallasto**, two remanence components were identified: an intermediate coercivity component KO1 pointing towards SW with positive inclination (D = 217.2°, I = 39.9°, N = 4, α_{95} = 19.8°) (Table 2; Figs 5A and 6) and a low-coercivity component KO2 directed down towards the NE (D = 29.6°, I = 33.3°, N = 9, α_{95} = 13.7°) (Table 2; Fig. 5B). Component KO1 is carried by magnetite and KO2 possibly by pyrrhotite. **Kalana** revealed only one remanence component (KA1), carried by magnetite or titanohematite. The component has relatively steep inclination declining towards the NE (D = 53.0°, I = 56.8°, N = 7, α_{95} = 7.8°) (Table 2; Figs 5C and 6). In **Anelema,** three distinct remanence components (AN1, AN2, and AN3) were identified. Component AN1 pointing towards the SW with moderate positive inclination (D = 217.8°, I = 32.6°, N = 11, α_{95} = 12.8°) (Table 2; Figs 5D and 6) is probably carried by magnetite. Component AN2 has SW declination and intermediate negative inclination (D = 225.4°, I = –27.8°, N = 13, α_{95} = 10.3°) (Table 2; Fig. 5E) and is likely carried by hematite. The SE directed component AN3 (Table 2) is of unknown origin and is not described furthermore here. The **Kurevere** samples carry only one component (KU1) with a SW declination and positive inclination (D = 249.3°, I = 27.1°, N = 4, α_{95} = 9.8°) (Table 2; Figs 5F and 6). The carrier of this magnetization is probably magnetite.

Components AN1, KO1, and KU1 are all likely carried by magnetite. Because their remanence directions are close to each other (Fig. 6), it is possible that they represent magnetizations of fairly similar age as is discussed later. Component AN2 is probably carried by hematite and component KO2 by pyrrhotite.

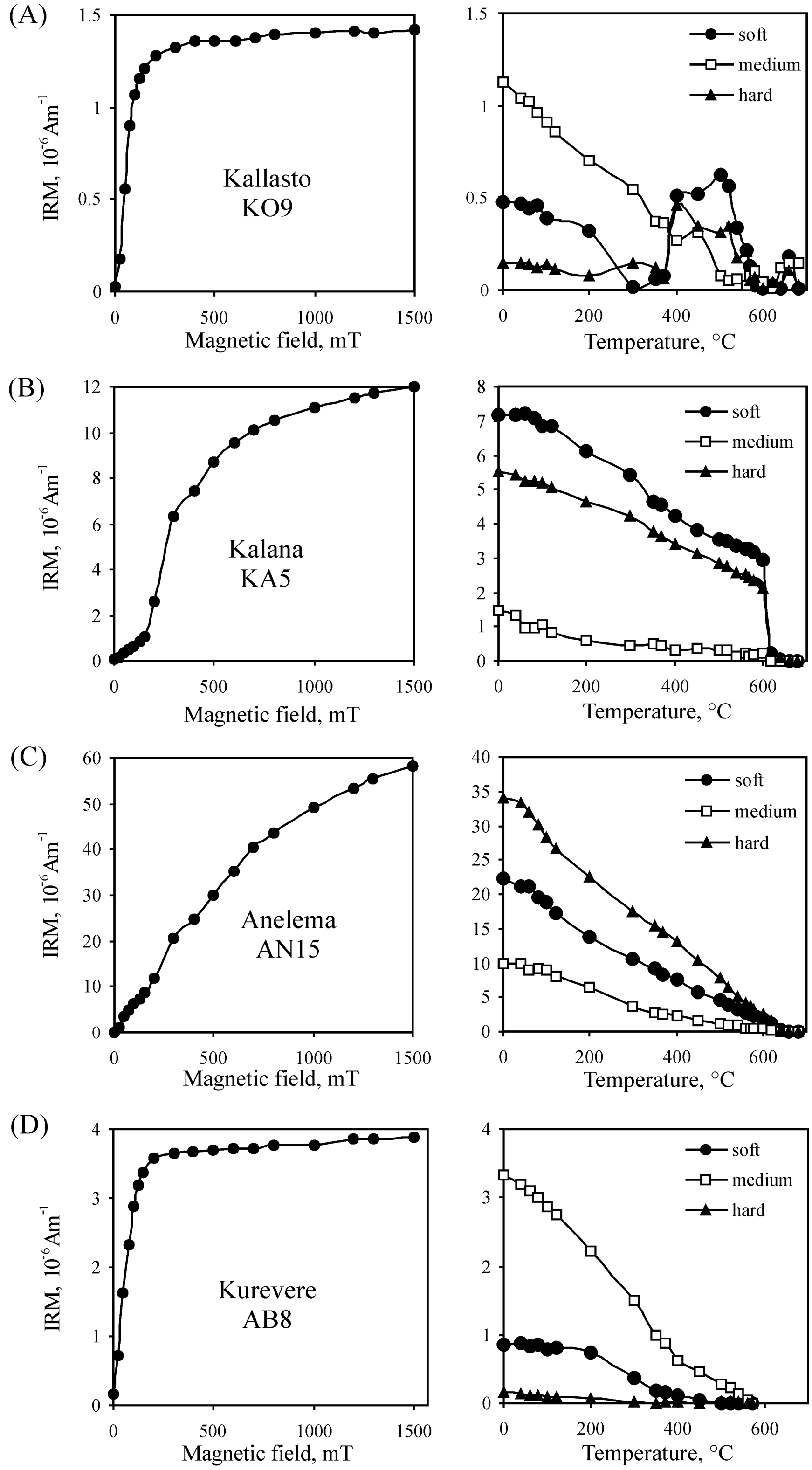

Fig. 4. Progressive acquisition of the IRM (left) and thermal demagnetization of a three-component IRM (right) produced by magnetizing sample in 0.12 T along the *x*-axis, followed by 0.4 T along the *y*-axis, and then 1.5 T along the *z*-axis for studied Silurian carbonates. The soft (<0.12 T), medium (0.12–0.4 T), and hard (0.4–1.5 T) components are shown during thermal demagnetization. Samples KO9 from Kallasto (A), KA5 from Kalana (B), AN15 from Anelema (C), and AB8 from Kurevere (D).

Table 1. Physical properties (mean values and standard deviations) of carbonates from the studied sites

Site	Number of specimens	Apparent density, kg m^{-3}	Magnetic susceptibility, $\times 10^{-6}$ SI	Intensity of the NRM, mA m^{-1}
Kallasto	86	2656 ± 10	–6 ± 9	0.03 ± 0.03
Kalana	125	2580 ± 102	4 ± 17	0.04 ± 0.05
Anelema	150	2655 ± 43	15 ± 9	0.07 ± 0.05
Kurevere	86	2587 ± 61	2 ± 10	0.07 ± 0.06

NRM – natural remanent magnetization.

Table 2. Characteristic remanence directions of studied carbonates and corresponding virtual geomagnetic pole positions calculated as mean of samples

Component	*N*	Polarity	Declination (*D*), °	Inclination (*I*), °	*k*	α_{95}, °	Plat, °	Plong, °	dp, °	dm, °
KO1	4	N	217.2	39.9	22.6	19.8	2.8	169.0	14.3	23.8
KO2	9	N	29.6	33.3	15.0	13.7	43.9	162.3	8.9	15.6
KA1	7	N	53.0	56.8	61.4	7.8	50.1	124.4	8.2	11.3
AN1	11	N	217.8	32.6	13.6	12.8	7.6	168.5	8.2	14.5
AN2	13	R	225.4	–27.8	17.2	10.3	34.8	147.5	6.2	11.3
AN3	16	N	139.7	55.2	25.0	7.5	10.2	56.8	7.6	10.7
KU1	4	N	249.3	27.1	89.3	9.8	1.9	138.4	5.8	10.6

N – number of samples revealing the component, *k* – Fisher's (1953) precision parameter, α_{95} – the radius of a cone of 95% confidence about the mean, Plat and Plong – latitude and longitude of the virtual geomagnetic poles, dp and dm – semi-axes of an oval of 95% confidence of the pole. Components from the Kallasto locality are KO1 and KO2; from the Kalana quarry KA1; from Anelema AN1, AN2, and AN3; from the Kurevere locality KU1.

DISCUSSION

Previous palaeomagnetic studies of sedimentary rocks in the Baltic region have shown that the remanences are mostly of secondary origin, residing in newly formed mineral phases, rather than residing in original minerals deposited during sedimentation (Katinas & Nawrocki 2004; Plado & Pesonen 2004; Plado et al. 2008). According to the present study, the carriers of the remanent magnetization are (i) allogenic and syn-sedimentary and/or early diagenetic authigenic iron-bearing minerals of the primary sedimentary siliciclastic and carbonate rocks and (ii) alteration products of primary minerals or new authigenic minerals formed during late-diagenetic, hydrothermal, or weathering processes. Secondary calcite and dolomite associated with sulphide (pyrite, galenite, sphalerite) as well as sulphate (baryte) mineralization have been found as fracture and pore fillings or in vertical fault-related zones within altered rocks (Pichugin et al. 1976; Puura et al. 1996, 1999; T. Pani pers. comm. 2007). In addition, secondary dolomitization occurs as large or local stratiform bodies, e.g. in Rõstla (Teedumäe et al. 2001) and Kurevere (unpublished data by V. Puura and T. Pani 2004).

All secondary NRMs are potential geological signals, which can record the earth's magnetic field during regional uplift, folding, igneous intrusion event or fluid penetration (Dunlop 1979). In our study different components from four locations were identified (Table 2 and Fig. 7). A similar SW pointing low/intermediate inclination remanence component was isolated both in the Kallasto (KO1) and Anelema (AN1) carbonates (Fig. 6). When palaeomagnetic poles, calculated from the remanence directions, are plotted on the APW path of Fennoscandia (Torsvik & Cox 2005) (Fig. 7), their ages point to the Silurian–Early Devonian. Based on their ages, the remanence is considered to be of syn-depositional or early diagenetic origin. From the Kurevere dolomites a slightly younger pole (KU1) was obtained. Scanning electron microscope studies of Kurevere dolomites have shown spheroidal aggregates, which are mostly composed of iron oxide that is replacing the early-diagenetic framboidal pyrite aggregate (Fig. 3). As other rock magnetic studies (IRM and Lowrie test;

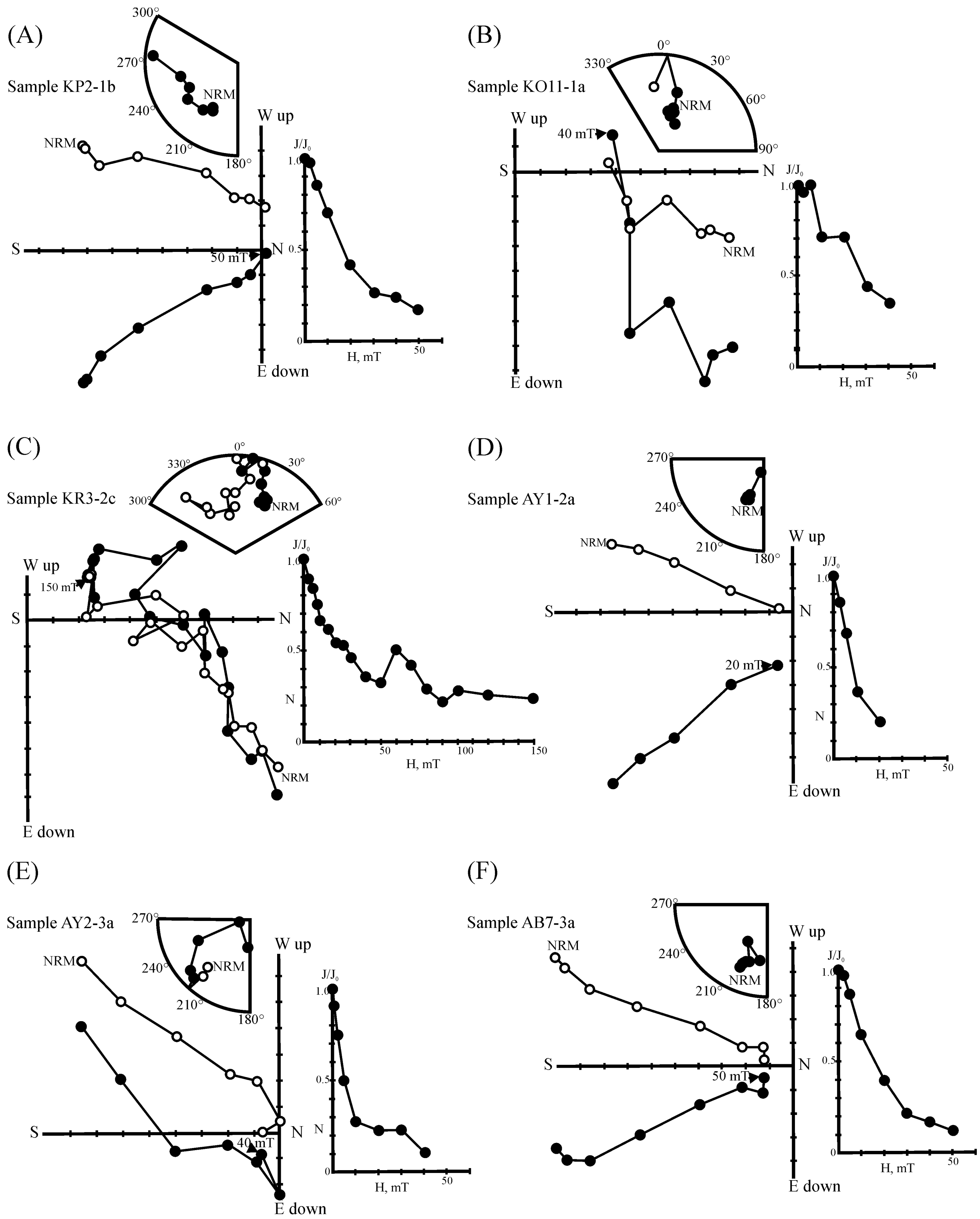

Fig. 5. Examples of AF demagnetization behaviour: KO1 and KO2 components from Kallasto (A, B); KA1 component from Kalana (C); AN1 and AN2 components from Anelema (D, E), and KU1 component from Kurevere (F). Filled and open symbols denote data projected onto the horizontal and vertical plane, respectively.

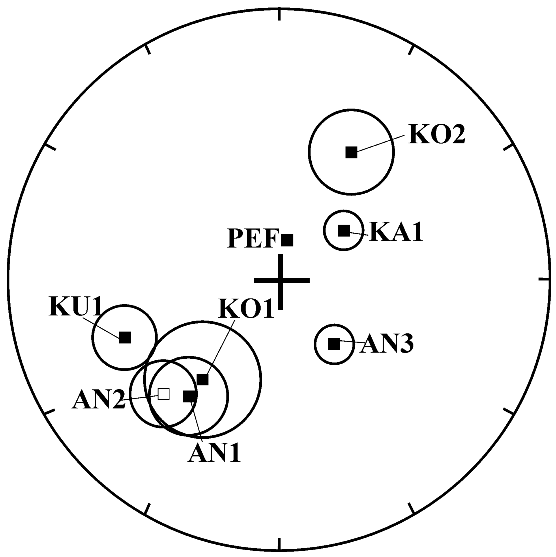

Fig. 6. Site mean palaeomagnetic directions. Circles indicate cones of α_{95} confidence about the means. PEF shows the direction of the present earth field in Estonia.

Fig. 4D) have shown only the presence of magnetite in Kurevere samples, we presume that the oxidation of pyrite to magnetite has taken place and late-diagenetic origin is the most likely explanation of this component. As shown before, in all three formations the carrier of the component (KO1, AN1, and KU1) is magnetite. The slight difference of poles between KU1 and KO1/AN1 may also be due to the low remanent magnetization of rocks, which causes scatter to the data. Signatures of rock dissolution and, locally, karst processes have been identified for this time span (Puura et al. 1999).

Jelenska et al. (2005) found similar magnetization from Wenlock carbonates in the Dniestr basin, Ukraine (IB; Fig. 7). They have considered the origin of this magnetization to be either primary or early diagenetic. There are some more indications of the secondary magnetizations of Early Devonian age from the igneous rocks of Kalak Nappe Complex, northern Norway (Torsvik et al. 1990) (A; Fig. 7). In the regional context, the ages of AN1, KO1, and KU1 of our study and IB (Jelenska et al. 2005) and A (Torsvik et al. 1990) magnetizations coincide with the Caledonian far-field deformation, uplift, and erosion (Puura et al. 1999).

A little younger remagnetization component of Late Devonian Mississippian age (pole RO1; Fig. 7) has been obtained also from Silurian carbonates (diagenetic dolomites) of the Rõstla quarry in central Estonia, where the magnetization is carried by magnetite and possibly by maghemite (Plado et al. 2008). It is suggested that this remagnetization was caused by low-temperature hydrothermal circulation due to the influence of the Caledonian or Hercynian orogeny.

The Anelema dolomites and Kallasto limestones carry also a late Palaeozoic remagnetization, AN2 and KO2, respectively. In Anelema, the AN2 component has reversed polarity, while in Kallasto the polarity of KO2 is normal. According to mineralogical studies, the carrier of AN2 is most likely hematite but the carrier of KO2 may be pyrrhotite (Fig. 4A). The cause for the secondary magnetization could be migration of low-temperature fluids when Baltica was affected by the post-folding processes of the Hercynian orogeny on its southern margin.

A Permian remagnetization has been observed also in some Ordovician carbonates in northern Estonia (Plado & Pesonen 2004) (component OR; Fig. 7) and in the Ordovician sequence of the St Petersburg area (Lubnina 2004) (component SP1; Fig. 7). In the St Petersburg area, the component is interpreted to be related to tectonic events at the Urals and in Western Europe (Lubnina 2004). Overprint (component HB; Fig. 7) of similar age has been revealed also from the Silurian carbonates of the Dniestr basin, Ukraine (Jelenska et al. 2005).

The remagnetization of the Kalana formation during the early Triassic (probably carried by titanohematite) may have been caused by a similar process as the Late Palaeozoic component in Anelema and Kallasto. As far as the intensities are quite low in all studied localities, the differences in pole positions may just reflect inaccuracy of data. Alternatively, the acquisition of magnetization took place during the Triassic, as a similar remanence has been obtained also elsewhere. A single remanence component with Triassic direction has been found from the Ordovician rocks in the St Petersburg area by Lubnina (2004) (component SP2; Fig. 7). This raises also the possibility that secondary magnetization of Kalana dolomites (KA1) could indicate an individual post-Palaeozoic remagnetization event.

The Late Palaeozoic secondary magnetization is a widespread worldwide phenomenon and the reasons for the formation of this kind of remagnetization have been related to different processes that took place during the formation and break-up of Pangea (Edel & Wickert 1991; Aifa 1993; Andersen et al. 1999; Grabowski et al. 2002; Zwing 2003; Preeden et al. 2007). Hydrothermal fluids may have caused alteration of pyrite as one of the most common original iron sulphide minerals in carbonate sediments. Alternatively, the remagnetization may have occurred due to the partial or complete oxidation of primary detrital or secondary magnetite.

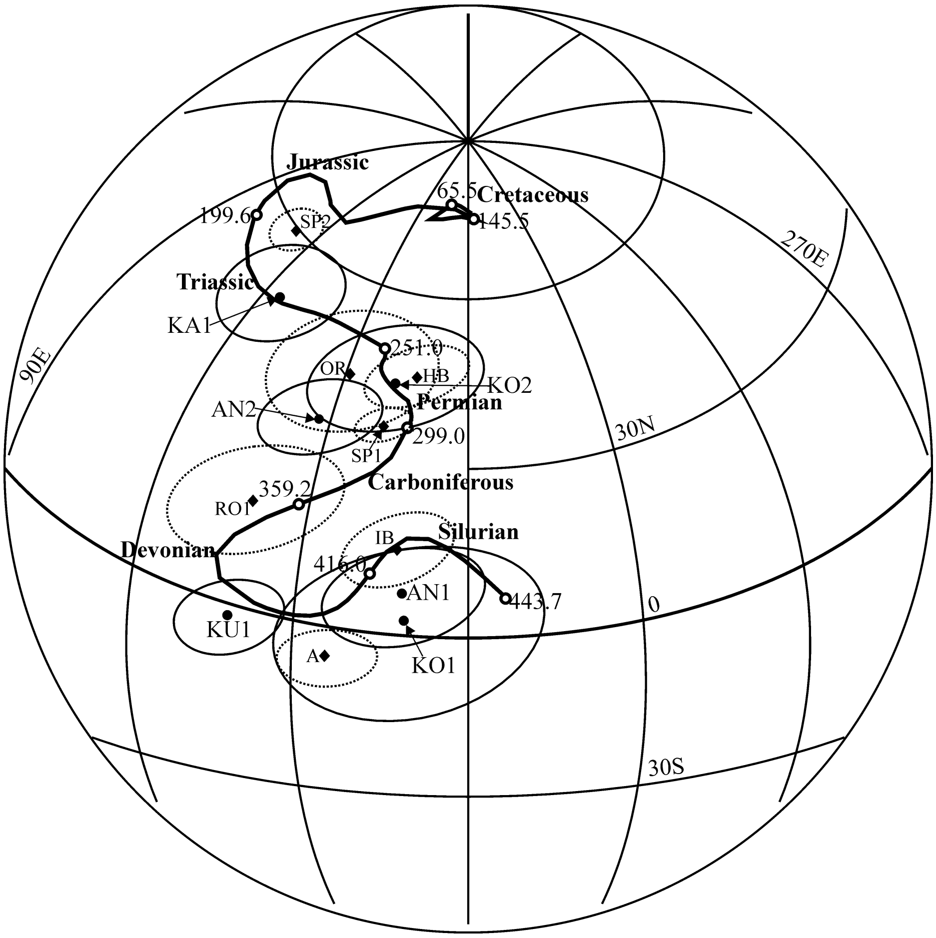

Fig. 7. The APW path for Baltica (Torsvik & Cox 2005) and poles found by our study (black dots with their α_{95} confidence circles): KO1 and KO2 from Kallasto; KA1 from Kalana; AN1 and AN2 from Anelema; KU1 from Kurevere. OR – from Ordovician rocks (Plado & Pesonen 2004) and RO1 from Silurian dolomites of Estonia (Plado et al. 2008); SP1 and SP2 are from Ordovician rocks of the St Petersburg area (Lubnina 2004); pole A from the study of Torsvik et al. (1990); IB and HB – from Silurian carbonates in the Ukraine (Jelenska et al. 2005). Further explanations and interpretation are in text.

Mineralogical changes in magnetic minerals and their remagnetizations in sedimentary formations during the Mid-Palaeozoic and Mesozoic to Cenozoic are still poorly studied in Estonia. The present data suggest a number of remagnetizations of different age in the region. Few well-defined common palaeomagnetic signatures are found in different localities. However, more palaeomagnetic studies are still needed in order to characterize the spatial and temporal patterns of remagnetizations. Together with precise mineralogical studies they may enable interpretations of mineralogical alterations in the rock massifs due to fluid flow, which are needed for the understanding of the latest tectono-thermal history of the region.

CONCLUSIONS

Silurian carbonates of Estonia revealed different components of magnetization. According to the mineralogical and rock magnetic studies, the components are carried by magnetite, (titano)hematite, and pyrrhotite.

The Silurian–Early Devonian syndepositional or early diagenetic component was revealed in the studied carbonates of the Anelema and Kallasto localities. A little younger remagnetization was found in diagenetically altered rocks of Kurevere by palaeomagnetic and mineralogical studies.

Late Palaeozoic and Triassic overprints were registered in Anelema, Kallasto, and Kalana. These are probably related to tectonically derived low-temperature hydrothermal fluids, activated during the processes related to the formation of the Pangea supercontinent.

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Sekundaarsed magnetiseeritused Eesti Siluri karbonaatsetes kivimites

Ulla Preeden, Jüri Plado, Satu Mertanen ja Väino Puura

Karbonaatkivimite jääkmagnetiseerituse käitumist mõõdeti neljast Kesk- ja Lääne-Eesti Siluri kivimeid avavast karjäärist. Uuriti Llandovery ja Wenlocki vanusega (444–423 miljonit aastat) kivimite 126 proovi. Uuringu käigus leiti, et kivimite primaarne magnetiseeritus on tõenäoliselt geoloogilise ajaloo vältel hävinud. Seetõttu eksisteerivad lubja- ja dolokivides peamiselt sekundaarse magnetiseerituse komponendid, mille kandjateks magnetmineraloogiliste uurimuste alusel on magnetiit, (titano)hematiit ning pürrotiit. Sekundaarse päritolu põhjused tulenevad setteaegsetest ja/või peatselt pärast settimist toimunud diageneetilistest muutustest ning hilisemast keemilisest jääkmagnetiseeritusest. Neist viimane viitab regionaalsetele sündmustele seoses superkontinendi Pangea moodustumisega Paleosoikumi lõpul.