



# Long-lived LREE mobility in the cratonic, rift and foredeep to foreland sedimentary cover at the western margin of the Karelia Province



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## ABSTRACT

The western margin of the Karelia Province of the Fennoscandian Shield consists of Archean crust covered by remnants of Paleoproterozoic (c. 2.5–1.9 Ga) metasedimentary rocks. The study area in the eastern part of the margin shows 2.3–2.1 Ga cratonic sedimentation followed by 2.1–2.05 Ga rift sedimentation and c. 1.91–1.92 Ga foredeep to foreland sedimentation related to continent–arc/continent collision. Extreme LREE mobility (loss up to >95% of La) is recorded by many samples from these units. Monazite, bastnäsite and, in some cases, allanite have been the prealteration LREE host phases in the LREE depleted samples. Monazite was altered to Th-silicates with variable loss of the LREE, the remaining part of which was incorporated in Th-poor monazite.

The depositional age of the sedimentary units was studied by dating (LA-MC-ICPMS) detrital zircon grains, and the age of LREE mobility by dating monazite and xenotime and by whole-rock Sm–Nd modeling. The maximum deposition age of the foredeep to foreland basin is 1.91–1.92 Ga based on detrital zircon data and the minimum age of the main foliation in the study area is 1.87–1.86 Ga based on the younger age limit of late-to post-tectonic xenotime and the ages of few probable metamorphic zircons. Coeval bastnäsite, with xenotime in a LREE enriched sample, suggests that this was also one important stage of LREE mobility. Monazite crystallizations have occurred 1.76–1.78 Ga ago while the Rb–Sr whole rock data suggest that the closure of this isotope system took place  $1732 \pm 21$  Ma ago. The Sm–Nd modeling gives ages at 0.4–1.0 Ga for LREE depletion. The Sm–Nd age of  $412 \pm 27$  Ma can be considered as the age of the latest major LREE depletion event.

We propose that alkali-bearing oxidizing fluids started to form in the cratonic sequences due to diagenetic reactions maybe as early as 2.3–2.1 Ga. Alkalinity of fluids was later increased by interaction with alkaline 2.05 Ga source materials before and during the c. 1.91–1.92 Ga foredeep to foreland basin stage. Basin inversion and metamorphic crystallization occurred at 1.91–1.87 Ga. Episodes of fluid migration at 1.78–1.73 Ga and afterwards were focused along fracture zones and in microfracture networks. The 0.4 Ga stage is the most prominent of the <1.7 Ga events and is best explained by assuming shield-scale foreland basin related to the Caledonian orogenic front, causing heat redistribution and also fluid circulation in the underlying crystalline basement. The 2.1 Ga formed marginal fault has been a very important shield-scale tectonic element and a pathway for fluid circulation for almost 2 billion years.

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## 1. Introduction

Taylor and McLennan (1985) have demonstrated that REE with Th and Sc in siliciclastic sequences are normally nearly quantitatively transferred from the catchment into the sedimentary budget due to the low aqueous solubility of these elements during weathering and transport. However subsequent diagenetic reactions, often involving the formation of authigenic monazite, may involve significant REE mobility and fractionation (Awwiller and Mack, 1991; Evans et al., 2009; Lev et al., 1999; Milodowski and Zalasiewicz, 1991; Ohr et al., 1991). In general REE are considered relatively immobile in most

hydrothermal processes and metamorphism but e.g. calc-silicate producing metasomatism and alteration during greenschist to amphibolite and granulite facies metamorphism can especially mobilize LREE (Gruau et al., 1992; Hansen and Harlov, 2007; Lahaye et al., 1995; Ordoñez-Calderón et al., 2008).

Extreme LREE mobility has occurred in some basins with extensive syn to postdepositional fluid migration and related dissolution of phosphate minerals (principally monazite). Examples include the Athabasca and Thelon basins in Canada (Gaboreau et al., 2007; Kyser et al., 2000; Renac et al., 2002), the Belt-Purcell basin in USA–Canada (González-Álvarez and Kerrich, 2010), McArthur basin in Australia (Gaboreau et al., 2005) and the Franceville basin in Gabon (Cuney and Mathieu, 2000; Mathieu et al., 2001). Sedimentary basins can have long post-depositional histories of episodic and protracted

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basinal fluid migration on the order of 600–1000 Ma (Alexandre et al., 2009; González-Álvarez et al., 2006; Rasmussen et al., 2007). This would imply long-term preservation of hydraulic conductivity in such basins and thus slow burial rates to prevent quick dewatering and recrystallization, which would have reduced the porosity significantly. Fluid migration can occur also in crystalline bedrock, along fracture zones, and in microfracture networks (Mercadier et al., 2010). Episodic fluid migration in crystalline bedrock has been documented from the Fennoscandian Shield (Sandström and Tullborg, 2009).

Unconformity-type U deposits vary from sediment-hosted, situated in the sandstones above the unconformity, to basement-hosted, situated below the basement–sediment unconformity. The U deposits are formed during post-depositional mineralization events, which may occur in successive episodes overprinted by several remobilization events (e.g., Alexandre et al., 2009; Mercadier et al., 2011). These are often related to the effects from far-field tectonic events. In many cases the alteration of monazite to a Th-silicate phase, due to oxidized and possibly alkaline fluids, has mobilized the U from monazite, with a later precipitation to a U ore due to the interaction of the U-bearing oxidizing basinal brines with basement-derived reducing fluids or reducing lithologies (Derome et al., 2005; Fayek and Kyser, 1997; Gaboreua et al., 2007; Hecht and Cuney, 2000). In some cases LREE-enriched aluminum phosphate-sulfate (APS) minerals are found around unconformity-type deposits (Gaboreau et al., 2005, 2007). In the Athabasca basin LREE depletion characterizes the lower sequences close to unconformity, balanced by LREE enrichment in the upper sequences (Gaboreua et al., 2007).

The western margin of the Karelia Province of the Fennoscandian Shield is comprised of Archean crust covered by remnants of Paleoproterozoic (c. 2.5–1.9 Ga) metasedimentary rocks, known as the Karelian formations (Fig. 1; Hölttä et al., 2008; Laajoki, 2005; Lahtinen et al., 2010). The Karelian cover sequence, which records 400–500 Ma of geological evolution, is dominated in its lower autochthonous parts by orthoquartzites and other epicontinental conglomeratic and arenitic rocks with mafic sills and minor volcanic interlayers (Kohonen and Marmo, 1992; Laajoki, 2005). In the study area these sequences dominate in the east whereas deep water graywackes and mudstones dominate in the west (e.g., Ward, 1987, 1988). The most voluminous occurrence of cratonic sequences is found in the Koli-Kontiolahti area (Kohonen, 1995; Kohonen and Marmo, 1992) where many small low-grade U occurrences are present (Fig. 1).

Already in the early 1990's it was detected that some meta-sedimentary samples from the Koli-Kontiolahti area (e.g. S51 in Fig. 1) had a disturbed Sm–Nd system. Later during the preparation of the paper by Lahtinen et al. (2010) it was noticed that many samples from the cratonic sequence in this area, and also the metapelites and metapsammities immediately west of it, showed a severe loss of LREE. Further, it was found, based on the screening of the nation-wide rock geochemical data base (Rasilainen et al., 2007), that samples from the metagraywackes and metapelites west of the Koli-Kontiolahti area (Fig. 1) did not show such LREE depletion. To further research the case, new samples were taken for this study in 2008 and 2010, mainly from traverses across the area where LREE depletion had been observed (Fig. 2).

The nature of the contact between arkosic-quartzitic strata in the east and the metapsammitic–pelitic strata in the west (Fig. 2) has been long debated. Most of the quartzites in the east have been intruded by mafic dikes (2.2–1.97 Ga, Vuollo and Huhma, 2005) but some quartzites close to the contact, in the upper part of the Puso Fm, and the metapelites and metapsammities to the west of them are devoid of these dikes. There are conglomerates along the contact marking a long-lived marginal fault but not an unequivocal basal contact of the westerly strata (Kohonen, 1995). Thus, the contact between quartzites and meta-arkoses with the metapelites and metapsammities is a major unconformity and/or major fault.

In this study we will assess the depositional age of the metapelites and metapsammities in the Koli-Kontiolahti area using LA-MC-ICPMS U–Pb analyses of detrital zircon grains, and the age of LREE mobility by dating monazite and xenotime and by Sm–Nd modeling. The chemical composition of the rock samples and the REE- and Th-bearing minerals is used to constrain the regional variation in primary rock compositions, their alteration and variation in alteration fluid chemistry, and whether there would be any link between LREE mobility and U occurrences. We also discuss the implications from these new results with respect to ideas regarding the general tectonic framework of the western margin of the Karelia Province. As all the studied sedimentary rocks are metamorphosed, mainly under upper greenschist to lower amphibolite facies conditions, the prefix ‘meta’ has been dropped.

## 2. Geological setting and sampled units

### 2.1. Geological setting

The northern and eastern part of the Fennoscandian Shield is composed mainly of Archean crust. The central part of the Archean block is the Karelia Province (Fig. 1; Hölttä et al., 2008). In the southwest, the Karelia Province is bound across a cryptic suture zone (Koistinen, 1981) to the Paleoproterozoic Svecofennian Province (c. 1.9–1.8 Ga) consisting of the composite Svecofennian Orogen (Lahtinen et al., 2005). Multiphase intraplate rifting and major mafic igneous activity in the Karelia Province occurred at 2.44, 2.22, 2.14–2.10 and 2.06 Ga, with mafic dikes at 2.3 and at 1.96 Ga (Hanski et al., 2010; Huhma et al., 2011; Laajoki, 2005; Vuollo and Huhma, 2005).

Deep chemical weathering possibly occurred over large areas of the Karelia Province, especially in the early Paleoproterozoic (Marmo, 1992). Prior to 2.2 Ga, erosion of the resultant paleosols led to fluvial, delta, and paralic type sedimentation of conglomerates and thick successions of quartz arenites (Laajoki, 2005). The 2.2 Ga layered intrusions and sills (Hanski et al., 2010) intruded both the basement and these sedimentary rocks. All carbonate deposits at 2.2–2.1 Ga (not preserved in Koli-Kontiolahti area) show a large positive  $\delta^{13}\text{C}$  isotope anomaly during the Lomagundi–Jatuli Event (Karhu, 1993; Melezhik et al., 2007 and references therein). Next, a ca. 2.1 Ga magmatic event occurs mainly as dike swarms (Vuollo and Huhma, 2005) at the present erosion level. Related attempted thinning of Archean crust is seen as mafic c. 2.1 Ga volcanic rocks and rift related sedimentary rocks, e.g., in the Tohmajärvi area (T in Fig. 1). Simultaneously a marginal-fault formed (Fig. 1).

The termination of a perturbation in the global carbon cycle occurred at ca. 2.06 Ga (Karhu, 2005; Melezhik et al., 2007). A thin veneer of 1.95 Ga oceanic crust formed on Archean subcontinental lithospheric mantle at the western margin (Peltonen, 2005). A characteristic feature of the southwestern margin of the Karelia Province is the thick successions of monotonous <1.94–1.92 Ga turbidites (Lahtinen et al., 2010), which are often allochthonous with tectonically enclosed fragments of 1.95 Ga ophiolite bodies (Fig. 1). Terms used for these deep sea turbidite sequences include monotonites (traditional field name), Upper Kaleva (Kontinen, 1987) and Western Kaleva (Kohonen, 1995).

Continent–arc/continent collision (c. 1.9 Ga) between the Archean craton and a Paleoproterozoic microcontinent–arc collage is the presently favored model for the junction at the western edge of the Karelia Province (e.g. Gaál, 1990; Kohonen, 1995; Lahtinen et al., 2005) but a back-arc/retro-arc basin (e.g. Gaál, 1986; Hietanen, 1975) or an accretion of arc terranes along a strike-slip (e.g. Park, 1985) or as an accreted arc collage along a strike-slip (Kontinen and Paavola, 2006) has also been proposed. Anyhow a fold and thrust belt formed (Fig. 1) along the craton margin in which early thin skin thrusting was followed by thick skin thrusting involving basement (Kohonen, 1995; Koistinen, 1981; Sorjonen-Ward, 2006; Ward, 1987). The age of thrusting can be bracketed between c. 1.92 Ga and 1.87 Ga

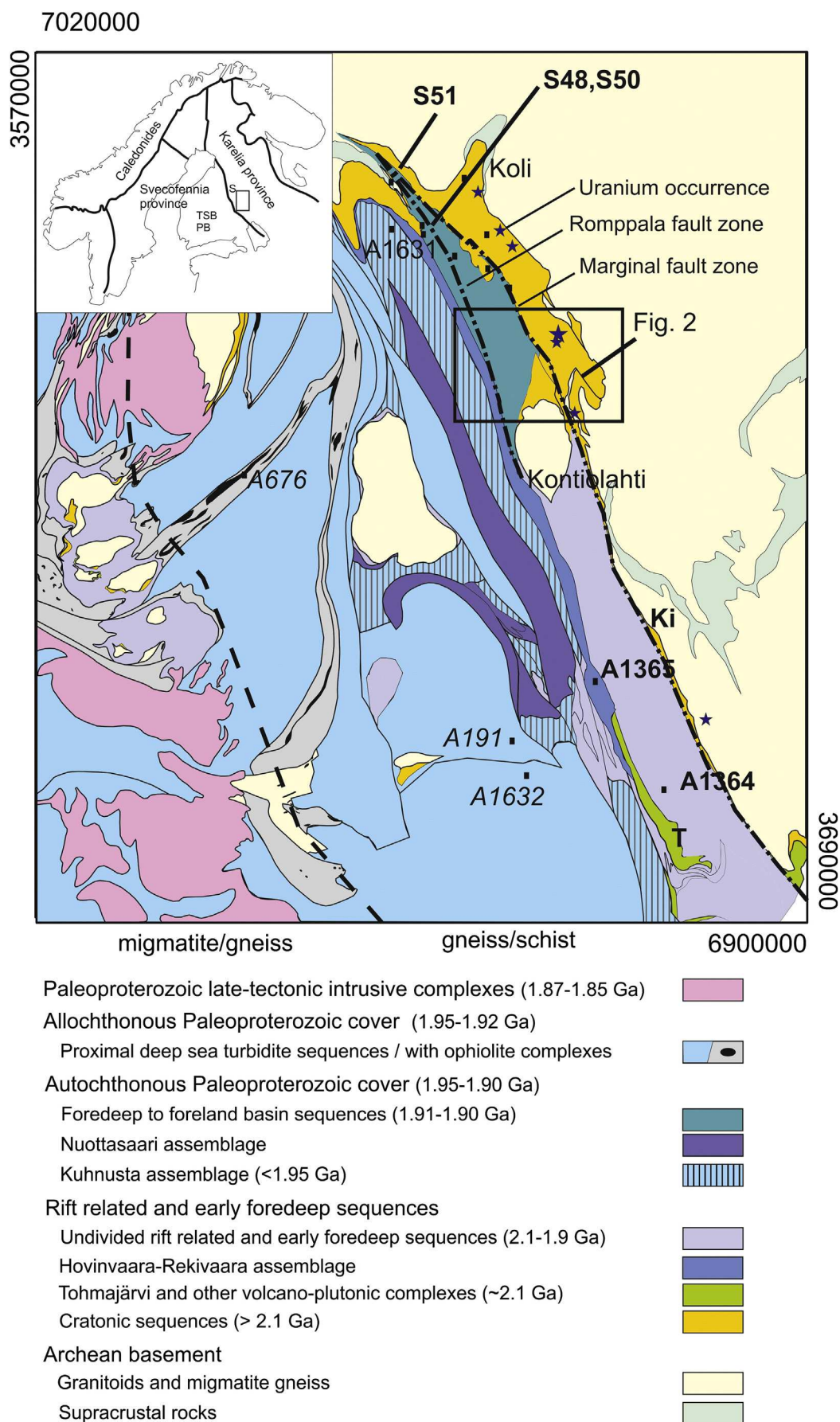


**Fig. 1.** A geological map of the Eastern Finland modified from a *Bedrock of Finland – DigiKP*. Sample numbers refer to [Lahtinen et al. \(2010\)](#) (italics) and to [Table 1](#) (bold). Dashed line approximates the onset of migmatization.

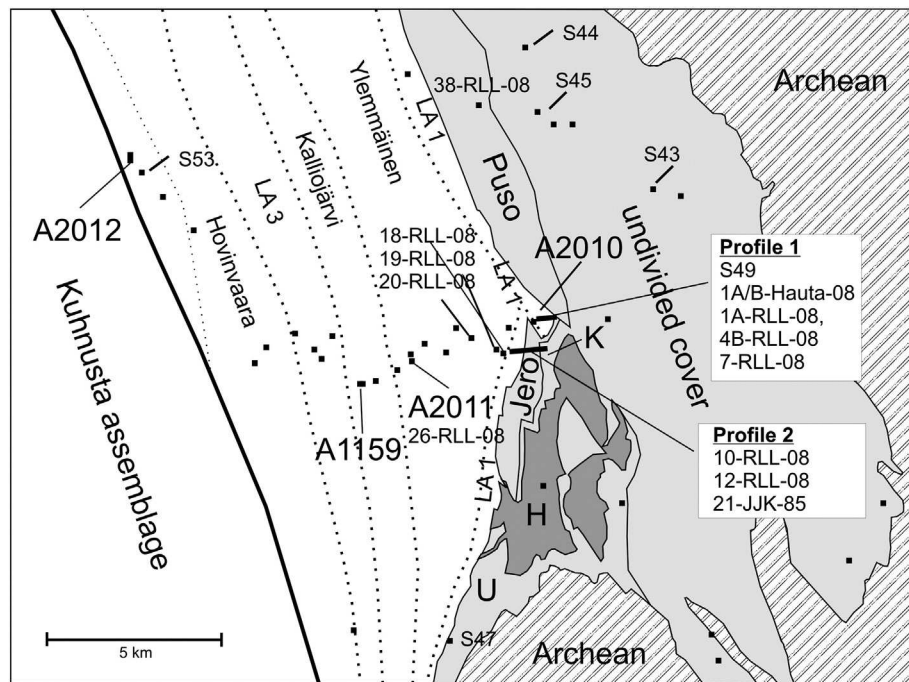


**Fig. 2.** A map of the study area. Sample numbers refer to Table 1. Division into Hokkalampi paleosol (H), Urkkavaara Formation (U), Koli Formation (K), Jero Formation (Jero) and Puso Formation (Puso) are from Kohonen and Marmo (1992). Division into lithological assemblages and lithotype are from Kohonen (1995).

based on the youngest detrital zircons in the deep sea turbidite sequences and cross-cutting granites, respectively (Huhma, 1986; Lahtinen et al., 2010). Peltonen et al. (2008) favored the initiation of thrusting at the latest at c. 1.90 Ga.

## 2.2. Geology of the study area and sampled units

The basal cover in the Koli-Kontiolahti area consists mainly of talus breccias, polymict conglomerates, and glaciogenic rocks (with dropstones and diamictites in the Urkkavaara Fm, Fig. 2; Kohonen and Marmo, 1992). An extensive paleosol (Hokkalampi Paleosol, Marmo, 1992; Fig. 2) formed within the basement and the early cover became buried below quartz pebble conglomerates and chemically mature, at least partly aeolian, quartzites of the Koli Formation (e.g. S43 in Fig. 2). Alluvial conglomerates and arkoses of the subsequent Jero Formation (e.g., S44 and S45 in Fig. 2) deposited both on the earlier sediments and basement. The Jero Formation is overlain by thick dominantly fluvial quartzites of the Puso Formation (Fig. 2) having also some clastic K-feldspar. These units are all cut by 2.2 Ga mafic sills (Pekkarinen et al., 2006; Vuollo and Huhma, 2005) with the exception of the upper part of the Puso Formation. The Puso Formation quartzites can be correlated with similar quartzites in Kiihtelysvaara (Ki in Fig. 1), there capped by 2.1 Ga mafic volcanic rocks (Pekkarinen and Lukkarinen, 1991). In summary, we may assume that the cratonic sequences in the Koli-Kontiolahti area (Fig. 2) are >2.1 Ga in age (cf. Pekkarinen et al., 2006).

The heterogeneous pelite–psammite associations west of the cratonic sequences (Fig. 2) have been studied in detail by Kohonen (1995). He divided the area into lithological assemblages (LA 1 to LA 5) with characteristic lithotypes. He noticed that the LA 5 turbidites (Kuhnusta assemblage in Fig. 1) were similar to those found in the deep sea turbidite sequences more to the west. This interpretation was later verified by geochemistry (Lahtinen, 2000; cf. Kohonen, 1995) and the age spectrum of detrital zircons (Lahtinen et al., 2010). The absence of ophiolitic bodies and the occurrence of channel fill conglomerates in the basal part of the formation (Kohonen, 1995; Ward, 1987, 1988) favor an autochthonous to parautochthonous setting for the Kuhnusta assemblage. Magnetic anomalies related to the 2.2 Ga sills extend (ghostlike) from the east below the whole LA1-Ylemmäinen–Kalliojärvi area (especially

in its middle part in Fig. 2) indicating that the rock prism preserving these units was very thin.

The assemblages LA 1, LA 2, and LA 3, and the Ylemmäinen and Kalliojärvi lithotypes of the LA 4 are now interpreted as part of the foredeep to foreland basin sequence of the continental arc/continent collision at c. 1.9 Ga (this study). The arkoses of the Hovinväara lithotype (LA 4) have been correlated with the arkoses from Rekivaara in Tohmajärvi (A1365 in Fig. 1). The deposition age for the arkoses is  $\leq 2.1$  Ga based on the age of syn-volcanic gabbro sill ( $2105 \pm 15$  Ma, Huhma, 1986) in Tohmajärvi (T in Fig. 1). The sedimentary rocks between Kiihtelysvaara and Tohmajärvi (Fig. 1) have been interpreted in terms of an intracratonic rift basin fill (e.g., Ward, 1988) but a longer depositional history of up to 1.9 Ga seems possible. We have reanalyzed the Valkeasuo wacke detrital zircon age spectrum (A1364 in Fig. 1; see Lahtinen et al., 2010) to be able to compare this sample with those from the foredeep to foreland basin sequence in the Koli-Kontiolahti area.

The perhaps most distinctive unit in the Koli-Kontiolahti area is the discontinuous LA 1 along the margin of the cratonic sequences (Fig. 2). Contacts of the LA 1 are typically not exposed. The few contact exposures show sheared rocks with abundant multi-stage quartz veining. The contact zone partly coincides with the marginal fault (Fig. 1). The fact that the LA 1 dips more steeply than the cratonic strata (Pekkarinen et al., 2006) indicates that thrust faulting has occurred along the contact at some stage. A distinctive feature for the basal part of the LA 1 is pure quartzite interbeds, breccia-conglomerates with phyllite matrix (talus breccia?) and arkose-fragments in phyllites, which are found within the nearest 0–200 m from the basal contact with the quartzites, conglomerates, and arkoses of the cratonic sequences (Kohonen, 1995). This sequence favors an originally depositional contact. If this interpretation is correct, it suggests that inclined exhumation might have occurred before deposition as the LA 1 is in contact with the Puso, Koli, Jero, Hokkalampi, and Urkkavaara Formations (Fig. 2) and finally with the basement (Fig. 1) when coming from north (Puso) to the south.

Kohonen (1995) interpreted the LA 1 sequence to represent a distal shelf environment where the quartzite and carbonate interbeds were deposited from storm generated currents. Typically LA 1 shows thin

lamination from the mm-scale micaceous layers to sand-size cm-scale layers. Well-rounded quartz clasts are common but detrital biotite and rare K-feldspar clasts are also found. The maximum inferred thickness of LA 1 at Hautajärvi (profile 1 in Fig. 2) is 200–400 m. Within LA 1, the amount and the thickness of quartzite interbeds decrease upwards so that they finally disappear, whereas concurrently sandy-silty wacke interbeds rich in ilmenite and apatite appear and become increasingly more common (Fig. 2).

The Ylemmäinen lithotype is difficult to interpret. Both the distal deltaic/shallow marine and the deeper slope turbidite environments are possible (Kohonen, 1995). Quartz, plagioclase, and rock fragments are common as sand-granule size clasts. The Kalliojärvi lithotype has bedding features fitting to the turbidite concept. Although quartz grains with obvious original sedimentary clast boundaries do occur, the Kalliojärvi lithotype is extensively recrystallized and feels mechanically “harder”, based on experiences during hammer sampling, than the rocks of the Ylemmäinen lithotype. The Varparanta lithotype of LA 3 is dominated by a dark, slightly graphitic-sulfidic phyllite and was possibly deposited on the outermost part of a shelf (Kohonen, 1995).

The Hovinvaara lithotype includes psammitic (arenitic) bedsets of several meters in thickness. The Bouma Tae and Tabe sequences can be interpreted to represent proximal slope turbidites (Kohonen, 1995). K-feldspar and plagioclase are found in addition to quartz as clastic minerals.

The shortening of the rigid quartz-rich rocks of the cratonic sequences is seen as imbrications and duplex structures with some local ductile cross-folding (Kohonen, 1988). The sequences west of the cratonic sequences (Fig. 2) show east-vergent asymmetric folding accompanied by either thrust imbrication of basement or reactivation of horst structures along the basement-cover interface during the early stages of tectonic basin inversion (Kohonen, 1995). This was followed by sinistral shear folding with a SE plunging shallow fold axis (Kohonen, 1995). This later stage is seen on the meso- and microscale as crenulation and shearing, which is locally a prominent overprinting feature. Quartz veining and narrow zones of intensified shear (NNW) are also common. A distinctive feature cutting through the whole area is the Romppala fault zone (Fig. 1) which is a pyrrhotite-bearing, possibly a step-out, fault zone that, at least partly, follows lithological contacts. The youngest observable tectonic features are dextral NW–SE brittle strike slip faults which probably also have a dip slip component.

The metamorphic mineral assemblage biotite–chlorite–muscovite in the mica-rich rocks without any aluminum silicate porphyroblasts or their pseudomorphs indicates a rather low metamorphic grade. The locally very well preserved mm-scale lamination and clastic texture are in accordance with this. The association of kyanite/andalucite in the quartzites and albite–sericite–chlorite–biotite in the mica-rich variants of the cratonic sequence, indicates greenschist facies above the biotite isograd (Pekkarinen et al., 2006). Retrograde kaolinite and pyrophyllite characterize the later cataclastic stage (Marmo, pers. com.) and this parageneses indicates temperatures of around 400 °C (P. Hölttä, personal communication).

### 3. Sampling and analytical methods

The data set (Appendix 1; Figs. 1 and 2) includes samples from Kohonen (1995), samples from the Rock Geochemical Data Base (RGDB) of Finland (Rasilainen et al., 2007) and samples taken specifically for this study in 2008 and 2010. Samples from the RGDB were taken using a mini-drill and other samples were taken by a hammer. Samples with visible signs of surface weathering were rejected though few samples show signs of slight oxidation/leaching of sulfides and feldspar alteration. The Romppala fault zone and another fault at the western end of Profile 1 are enriched in sulfides and show distinct sulfide weathering, which is evident also in our samples.

Geochemical analyses were done in the laboratories of the Labtium Oy. Major elements and Ba, Cr, Cu, Ni, S, Sr, V, Y, Zn, and Zr were determined by XRF from pressed briquettes, and non carbonate C and CO<sub>2</sub> by a Leco CR-12 carbon analyzer. REE, Co, Nb, Hf, Rb, Sc, Ta, Th, and U were determined by ICP-MS from a solution combining those after dissolution of the sample (0.2 g) with hydrofluoric acid–perchloric acid and a lithium metaborate/sodium perborate fusion of the insoluble residue. More detailed description of the analytical methods, precision and lowest reliable concentration is found in Rasilainen et al. (2007).

Analytical techniques for Sm–Nd data have been described in Lahtinen and Huhma (1997). Sample dissolution was performed in sealed Teflon bombs. A mixed <sup>150</sup>Nd–<sup>149</sup>Sm spike solution was added to the sample prior to the dissolution. After careful evaporation of the fluorides, the residue was dissolved in 6 M HCl resulting in a clear solution. In older analyses (S28–S53), a mixed spike of <sup>145</sup>Nd–<sup>149</sup>Sm was added to an aliquot of the clear solution. Measurements were made on a VG SECTOR 54 mass spectrometer at the Geological Survey of Finland using Ta–Re triple filaments and a dynamic mode of measurements. Nd ratios are normalized to <sup>146</sup>Nd/<sup>144</sup>Nd = 0.7219. The long-term average <sup>143</sup>Nd/<sup>144</sup>Nd for the La Jolla standard is 0.511849 ± 0.000013 (standard deviation for 130 measurements during years 2008–2011). The Sm/Nd ratio of the spike was calibrated against the Caltech mixed Sm/Nd standard (Wasserburg et al., 1981). Based on duplicate analyses the error in <sup>147</sup>Sm/<sup>144</sup>Nd is estimated to be 0.4%. Initial <sup>143</sup>Nd/<sup>144</sup>Nd (epsilon) was calculated using the following parameters:  $\lambda^{147}\text{Sm} = 6.54 \times 10^{-12} \text{ a}^{-1}$ , <sup>147</sup>Sm/<sup>144</sup>Nd = 0.1966, and <sup>143</sup>Nd/<sup>144</sup>Nd = 0.512638 for present-day CHUR. T-DM was calculated according to DePaolo (1981).

For Rb–Sr analyses, a mixed <sup>87</sup>Rb–<sup>84</sup>Sr spike was added to the sample prior to dissolution. The concentrations were measured by isotope dilution, and chemical separations were carried out using standard chemical procedures involving cation-exchange procedure (7 ml of AG50Wx8 ion exchange resin in a bed of 12 cm length). The Sr measurements were made in a dynamic mode on a VG SECTOR 54 mass-spectrometer single Ta filament. Rb was measured on a Nu MCICPMS using the method by Waight et al. (2002). The estimated error in <sup>87</sup>Rb/<sup>86</sup>Sr is 1%. The <sup>87</sup>Sr/<sup>86</sup>Sr ratio is normalized to <sup>86</sup>Sr/<sup>88</sup>Sr = 0.1194. The average value for SRM987 is <sup>87</sup>Sr/<sup>86</sup>Sr = 0.710249 ± 18 (stdev, n = 100). Measurement of the rock standard BCR-1 provided values of Sm = 6.63 ppm, Nd = 28.88 ppm, <sup>143</sup>Nd/<sup>144</sup>Nd = 0.512640 ± 0.000015, Rb = 47.1 ppm, Sr = 330 ppm, and <sup>87</sup>Sr/<sup>86</sup>Sr = 0.70502 ± 0.00002. The average blank was 50 pg for Sm, 150 pg for Nd, and 300 pg for Sr. Procedures for LA-MC-ICPMS analyses on zircon followed the methods given by Mikkola et al. (2010).

Monazite and xenotime grains in the thin sections were located using back scattered electron (BSE) imaging on a SEM (JEOL JSM 5900LV) equipped with an element analyzer EDS (Oxford Instruments INCA/Feature analysis). The whole thin section area was scanned and the coordinates of grains with a diameter of 10 µm or more were recorded. Bastnäsite and thorite grains were simultaneously located. The coordinates were transferred to the electron microprobe (CAMECA SX100) for subsequent electron probe microanalysis (EPMA). EPMA of the most interesting grains was made using an accelerating voltage of 15 kV and with a probe current of 20 nA. The beam diameter was defocused to 5 µm. The analyses were corrected on-line using the matrix correction procedure PAP (Pouchou and Pichoir, 1986).

BSE and cathodoluminescence (CL) images were made of the identified monazite and xenotime grains in order to target the analysis spots. U–Pb dating analyses were performed using a Nu Plasma HR multicollector ICPMS at the Geological Survey of Finland in Espoo using a technique very similar to Rosa et al. (2009) except that a Photon Machine Analyte G2 laser microprobe was used. Samples were ablated in He gas (gas flows = 0.4 and 0.1 l/min) within a HeEx ablation cell (Müller et al., 2009). The He aerosol was mixed with Ar (gas flow = 0.8 l/min) prior to entry into the plasma. The gas mixture was optimized daily for maximum sensitivity.

All analyses were made in a static ablation mode. Ablation normal conditions were a 10  $\mu\text{m}$  beam for the monazite and a 5  $\mu\text{m}$  beam diameter for the xenotime with a pulse frequency of 5 Hz, and a beam energy density of 0.55 J/cm<sup>2</sup>. A single U–Pb measurement included 20 s of on-mass background measurement, followed by 30–60 s of ablation with a stationary beam. Masses 204, 206, and 207 were measured in secondary electron multipliers, and 238 in the extra high mass Faraday collector. The geometry of the collector block does not allow for the simultaneous measurement of <sup>208</sup>Pb and <sup>232</sup>Th. Ion counts were converted and reported as volts by the Nu Plasma time-resolved analysis software. <sup>235</sup>U was calculated from the signal at mass 238 using a natural <sup>238</sup>U/<sup>235</sup>U = 137.88. Mass number 204 was used as a monitor for common <sup>204</sup>Pb. In an ICPMS analysis, <sup>204</sup>Hg originates mainly from the He supply. The observed background counting-rate on mass 204 was ca. 1200 (ca.  $1.3 \times 10^{-5}$  V), and has been stable at that level over the last year. The contribution of <sup>204</sup>Hg from the plasma was eliminated by on-mass background measurement prior to each analysis. The age related common Pb correction (Stacey and Kramers, 1975) was used when the analysis showed common Pb contents above the detection limit. Signal strengths on mass 206 were typically  $>10^{-3}$  V, depending on the U content and the age of the zircon.

Two calibration monazite standards and one monazite standard were run in duplicate at the beginning and end of each analytical session, and at regular intervals during the sessions. Raw data were corrected for background, laser induced elemental fractionation, mass discrimination, and drift in ion counter gains. The data was reduced to U–Pb isotope ratios by calibration to concordant reference zircons of known age, using protocols adapted from Andersen et al. (2004) and Jackson et al. (2004). In-house monazite standards A49 (1874  $\pm$  3 Ma) and A1326 (2635  $\pm$  2 Ma; Hölttä et al., 2000) were used for calibration. A single in-house xenotime standard A1298 (1852  $\pm$  2 Ma; Pajunen and Poutiainen, 1999) was used for calibration. In-house monazite samples, such as A276 (1920  $\pm$  11 Ma, 1915  $\pm$  3 by TIMS) and A60 (1856  $\pm$  10 Ma, 1842  $\pm$  3 by TIMS), were used for quality control. The calculations were done off-line, using an interactive spreadsheet program written in Microsoft Excel/VBA by T. Andersen (Rosa et al., 2009). To minimize the effects of laser-induced elemental fractionation, the depth-to-diameter ratio of the ablation pit was kept low, and isotopically homogeneous segments of the time-resolved traces were calibrated against the corresponding time interval for each mass in the reference standard. To compensate for drift in instrument sensitivity and Faraday vs. electron multiplier gain during an analytical session, a correlation of signal vs. time was assumed for the reference zircons. A description of the algorithms used is provided in Rosa et al. (2009). Plotting of the U–Pb isotopic data and age calculations were performed using the Isoplot/Ex 3 program (Ludwig, 2003). All the ages were calculated with 2 $\sigma$  errors and without decay constants errors. Data-point error ellipses in the figures are at the 2 $\sigma$  level. The concordant age offset from ID-TIMS ages for several samples does not exceed 0.5%.

## 4. Results

### 4.1. Geochemistry

The effects of provenance, source weathering, grain-size sorting, alteration, and diagenesis on the geochemistry of metasedimentary rocks at the western margin of the Karelian Province have been discussed in several publications (Kohonen, 1995; Kontinen and Sorjonen-Ward, 1991; Lahtinen, 2000; Lahtinen et al., 2010). Samples showing strong LREE mobility were not included in Lahtinen et al. (2010). The LA 1 to LA 3 and the Ylemmäinen lithotype were also not represented in the data set. We discuss very briefly the geochemistry of the sedimentary rocks in the study area. Averages of geochemically homogeneous and well-mixed deep-sea turbidites west of the Koli-Kontiolahti area (Fig. 1; WK in Fig. 3; data from Lahtinen, 2000) and similarly homogeneous turbidites from the central part of the Svecofennian province

(Fig. 1; TSB + PB in Fig. 3; data from Lahtinen et al., 2009) are shown for comparison. The samples from the Koli-Kontiolahti area normally have higher CIA and lower Th/Sc and Th/Cr (Fig. 3) than the WK and TSB + PB averages, which favor different provenances.

The quartzites and arkoses from the cratonic sequence show high CIA, due to a highly weathered source (paleosol), and often very high Th/Sc and Th/Cr ratios, indicating, apart a felsic source, a loss of ferromagnesian minerals during winnowing and/or transport. The LA 1 samples have a bimodal distribution of SiO<sub>2</sub> contents reflecting the occurrence of quartzite-interbeds in LA 1 phyllites. The westernmost (uppermost) part of profile 1 (Fig. 2) yielded several LA 1 samples showing lower CIA and Th/Cr (1-RLL-08 in Fig. 3) and also higher TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, REE, Nb, and Zr relative to other LA 1 samples at similar SiO<sub>2</sub> (Appendix 1). Characteristic features of LA 1 to LA 3 are high CIA and low Th/Cr.

Samples from the Ylemmäinen lithotype have a less weathered (lower CIA) and, in general more felsic source (higher Th/Sc and Th/Cr) than samples from LA 1 to LA 3. The Kalliojärvi lithotype resembles LA 1 to LA 3 in Th/Cr but is intermediate between them and the Ylemmäinen lithotype in Th/Sc and CIA. The Hovinväara arkose and psammite samples differ from the cratonic sequence samples in having a lower CIA and Th/Sc ( $\sim$ 1). The pelitic samples from Hovinväara have a very low Th/Cr and a high CIA similar to those in LA 1 to LA 3.

The Th–La diagram shows (Fig. 3) that La depletion is a characteristic feature of most samples in the study area. This is seen also in the psammite-normalized (Western Kaleva) REE patterns for LA 1 phyllites (Fig. 4) where the ultimate LREE depletion (e.g., 21-JJK-85) indicates  $>95\%$  loss of La. The LREE depletion affects also MREE to some degree. It seems that Dy–Ho is the turning point so that the heavier REEs are not affected, at least not in a detectable amount. Some LREE depleted samples have a positive Ce anomaly but it seems that even in these cases most of the originally present Ce has been lost. Also Eu behaves differently and shows less depletion than Gd and Sm (Fig. 4). Samples A2011 and 26-RLL-08, taken 20 cm apart from same unit, show LREE enrichment and a negative Ce anomaly, and LREE depletion and a positive Ce anomaly, respectively.

### 4.2. Sm–Nd and Rb–Sr data

The Sm–Nd isotopic data are given in Table 1 with the average U–Pb zircon ages, when available. In order to allow for a straightforward comparison an age of 1.9 Ga has been used in calculating the  $\epsilon_{\text{Nd}}$ -values for all the samples. The range in Sm/Nd ratios is wide with <sup>147</sup>Sm/<sup>144</sup>Nd ranging from 0.099 to 0.354. The calculated crustal residence age ( $T_{\text{DM}}$ ) ranges from 2.14 to 8.40 Ga and the  $\epsilon_{\text{Nd}}$  (1.9 Ga) values range from 0.3 to  $-53.9$ . Extreme values are caused by the observed LREE mobility leading to a disturbance in the Sm–Nd system.

The Th/La ratio of 0.3 (Fig. 3) is typical for Archean and Paleoproterozoic siliciclastic sedimentary rocks ( $0.27 \pm 0.04$ ; Mathieu et al., 2001). Sedimentary rocks, having Th/La ratios close to 0.3, an upper crustal <sup>147</sup>Sm/<sup>144</sup>Nd, and no clear Ce anomaly, can be considered as non-altered. There are few samples within this study that fulfill these criteria. The LA 1 sample 1A-Hauta-08 from a quartzite interbed has an  $\epsilon_{\text{Nd}}$  (1.9 Ga) of  $-5.1$  and a  $T_{\text{DM}}$  of 2552 Ma which are considered to represent source characteristics. Samples 1A-RLL-08 and A2010 have  $\epsilon_{\text{Nd}}$  (1.9 Ga) values of  $-1.3$  and  $-0.8$ , and  $T_{\text{DM}}$  values of 2354 Ma and 2279 Ma. LA 3 sample has an  $\epsilon_{\text{Nd}}$  (1.9 Ga) of  $-2.9$  and a  $T_{\text{DM}}$  of 2425 Ma.

Sample A2011, with LREE enrichment, and an  $\epsilon_{\text{Nd}}$  (1.9 Ga) of 0.3 and a  $T_{\text{DM}}$  of 2135 Ma could characterize the mobile LREE component. The Kalliojärvi sample S28 has an  $\epsilon_{\text{Nd}}$  (1.9 Ga) of  $-3.6$  and a  $T_{\text{DM}}$  of 2485 Ma. The Valkeasuo wacke (A1364; Lahtinen et al., 2010) has an  $\epsilon_{\text{Nd}}$  (1.9 Ga) of  $-6.3$  and a  $T_{\text{DM}}$  of 2721 Ma. The least altered samples S45 and 38-RLL-08 from the cratonic sequence show slight negative and positive Ce anomalies, while their Sm–Nd isotopic data infer a dominant Archean source component. The Rb–Sr isotopic data for

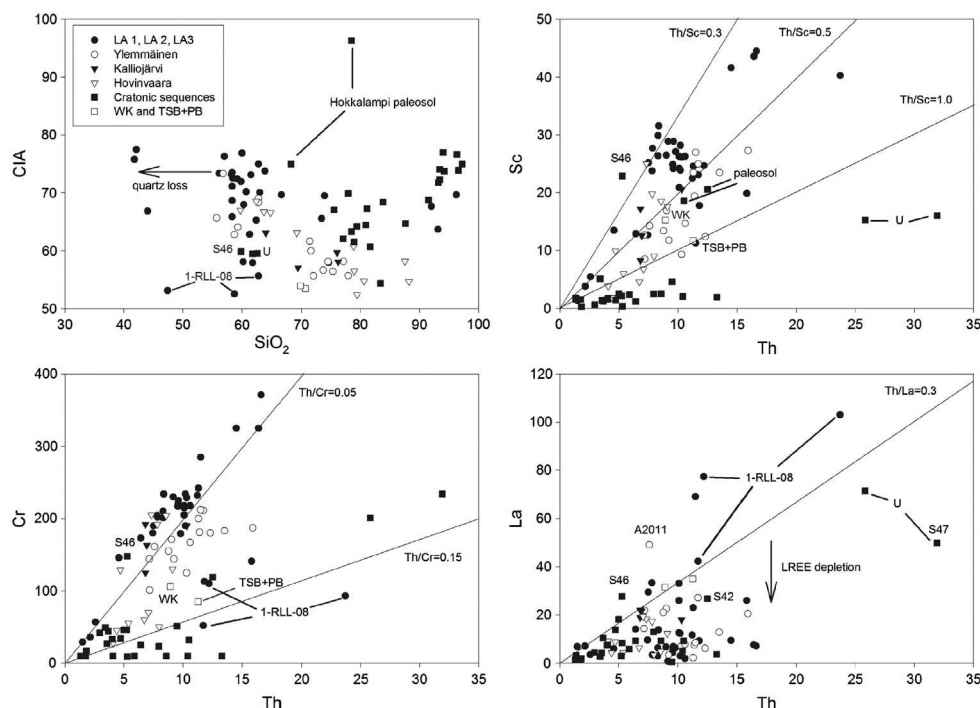


**Fig. 3.** Plots of CIA (Chemical index of alteration; Nesbitt, 2003 and references therein) vs.  $\text{SiO}_2$ , and Sc, Cr and La vs. Th. WK, Western Kaleva sedimentary rock average (Lahtinen, 2000) and TSB + PB, Tampere Schist Belt and Pirkanmaa Belt sedimentary rock average (Lahtinen et al., 2009). Abbreviations for samples (Table 1). U, Urkkavaara.

S48 and S51B/C/D (Fig. 1) are given in Table 2 and the calculated isochron is shown in Fig. 5. The  $1732 \pm 21$  Ma age represents the closure of the whole rock Rb–Sr system in the sampling area.

#### 4.3. Zircon data

Samples from LA 1 (A2010), the Ylemmäinen lithotype (A2011), and the Hovinvaara lithotype (A2012) were carefully chosen to characterize these units. Sample A1159, from the Kalliojärvi lithotype, has already been analyzed by SIMS (NORDSIM) and sample A1364 has been analyzed by TIMS (Lahtinen et al., 2010). Our main objective here is to study the age population of the detrital zircon grains, and to determine a maximum sedimentation age for each of the sampled units. All the LA-MC-ICPMS data are presented in Appendix 2.

The arkose sample A2012 from the Hovinvaara lithotype has 46 analyses (Fig. 6) on 39 grains which all are Archean. There is a clear maximum at 2.83 Ga and a broad maximum at 2.71–2.78 Ga. The Valkeasuo wacke A1364 (Fig. 1) has 62 analyses on 60 grains of which 8 are Proterozoic (Appendix 2; Fig. 6). Both the Archean and Proterozoic grains in this sample show oscillatory zoning and are typically very well rounded. Analytical errors are large, i.e. 40–50 Ma ( $2\sigma$ ) and the analyses are often discordant. The Archean population shows a large variation from 2.7 Ga to 3.0 Ga with a maximum at ca. 2.83 Ga. The seven youngest grains from 2.01 to 2.09 Ga could be within the error limits from same source and we propose 2.04–2.05 Ga as the maximum deposition age for this rock.

Sample 1A-RLL-08 is from a Zr-rich (Zr 491 ppm) fine sand-silt layer from the inferred uppermost part of the profile 1 (Fig. 2). To obtain zircon grains from this rock a new sample from an adjacent layer was taken (A2010). Sandy silt in A2010 is more quartz-rich and coarser grained than in 1A-RLL-08 but contains still 297 ppm of Zr and has also other geochemical characteristics akin to 1A-RLL-08 (Table 1 and Appendix 1). The zircon yield was low, probably due to a fine size of the grains ( $<100 \mu\text{m}$ ) occurring dominantly as minute inclusions within the micas. The obtained grains are mostly well-rounded and often show oscillatory zoning. Forty of the 50 analyzed grains were Archean and 60% of these plot between 2.68 and 2.75 Ga with a clear maximum

at c. 2.72 Ga. There are 11 analyses from 10 Proterozoic grains (Fig. 7) having an age span from 2.2 to 1.9 Ga. Two analyses from grain 27 and analyses from grains 6 and 43 define a maximum deposition age of 1.92–1.91 Ga.

Forty three zircon grains were analyzed from the representative psammite A2011 from the Ylemmäinen lithotype (Fig. 2). Although some grains are well ground most of them show well preserved prismatic tips. The zircon age spectrum differs from A2010 (Fig. 7) as now 28 grains are Proterozoic and only 15 Archean. The Archean population is small but 10 out of 15 grains have ages exceeding 2.75 Ga without clear age clustering. The Proterozoic grains show an age span from 2.2 to 1.9 Ga with clusters at 1.91 Ga and 2.03 Ga. Another characteristic feature is the lack of 1.95–2.0 Ga zircons. Two analyses from grain 31 have ages of  $1876 \pm 20$  Ma ( $2\sigma$ ) and  $1917 \pm 18$  Ma ( $2\sigma$ ) (Appendix 2). Grain 27 has an age of  $1887 \pm 18$  Ma ( $2\sigma$ ) and grain 32 an age of  $1857 \pm 20$  Ma ( $2\sigma$ ). A maximum deposition age of 1.91 Ga is confirmed.

Older SIMS data on A1159 graywacke from the Kalliojärvi lithotype comprise 15 Archean grains of which 12 are  $<2.75$  Ga (Lahtinen et al., 2010). We have 66 new analyses for this sample (Fig. 8), on 59 grains of which 7 are Proterozoic (Appendix 2). Zircons vary from well rounded to prismatic. The Archean population is dominated by  $<2.75$  Ga grains (78%) and the 13 analyses from the 7 Proterozoic grains vary from 2.2 Ga to 1.85 Ga. Grain 34 has a  $1915 \pm 14$  Ma ( $2\sigma$ ) core, whereas two analyses from the rim yield  $1881 \pm 10$  Ma ( $2\sigma$ ) and  $1858 \pm 10$  Ma ( $2\sigma$ ). Grain 57 has two analyses at  $1871 \pm 12$  Ma ( $2\sigma$ ) and  $1849 \pm 12$  Ma ( $2\sigma$ ), and grain 27 two analyses at  $1942 \pm 12$  Ma ( $2\sigma$ ) and  $1907 \pm 10$  Ma ( $2\sigma$ ). The maximum deposition age is difficult to interpret due to lack of a clear age cluster but an age about 1.91–1.92 Ga is proposed. The younger ages are possibly due to metamorphic–hydrothermal effects.

#### 4.4. Microprobe data

Altogether 45 polished thin sections from 42 samples were scanned by an electron microprobe for REE- and Th-rich minerals. The minerals found are listed in Table 3 and selected analyses are

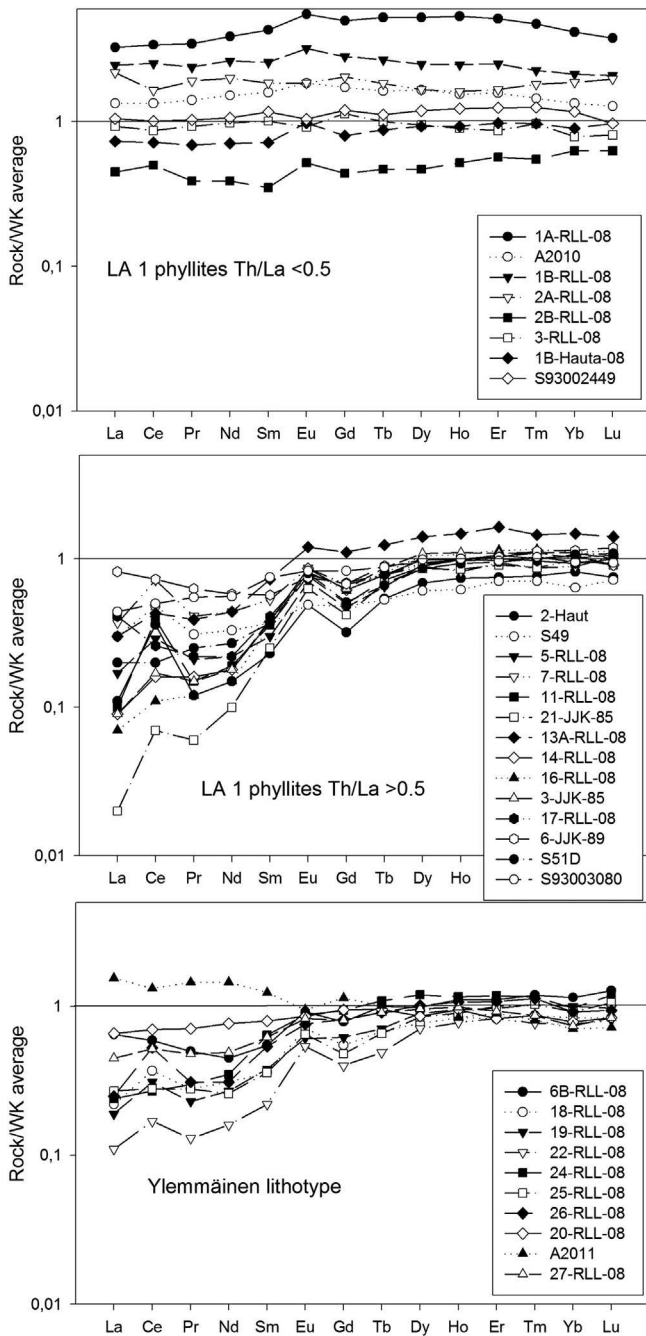


Fig. 4. Psammite-normalized (Western Kaleva; Lahtinen, 2000) REE patterns for selected samples in this study. Sample numbers refer to Table 1.

listed in Table 4. Three polished thin sections were made from LREE-enriched sample A2011. The lack of LREE minerals in two of them indicates a heterogeneous occurrence of these accessory minerals.

The non-LREE depleted LA 1 quartzite 1A-Hauta-08 (Table 3) contains allanite but otherwise monazite and bastnäsite are the sole LREE-rich minerals in the studied samples. Bastnäsite is found in LA 1 and the Ylemmäinen lithotype samples. High-Y bastnäsite is the only LREE-rich mineral in the anomalous sample 1A-RLL-08. Bastnäsite occurs mostly as minute crystals ( $<10\ \mu\text{m}$ ), some included in albite and quartz, and also in large aggregates of coarse grains (Fig. 9). There is a great variation in Y and Th contents between the different bastnäsite varieties (Table 4). Xenotime has been found in three samples from the Ylemmäinen lithotype (Tables 3 and 4, and Fig. 9). Th-silicates have been found in all LREE-depleted samples. In one it occurs surrounded by a carbonaceous matter (thucolite).

Monazite has been found in few cases as inclusions in detrital quartz (e.g. 38-RLL-08 in Fig. 9) but normally it occurs as minute crystals ( $<10\ \mu\text{m}$ ) or slightly larger grains (Fig. 9). One monazite grain (18-RLL-08) occurs in a thin quartz–mica vein (Fig. 9) that crosscuts the foliation. Thorium values in the monazites vary from 0.1% in grain 1a from sample 1A-Hauta-08 to 10.8% in a monazite inclusion in quartz from 38-RLL-08. Typically U values are low.

#### 4.5. U–Pb data on monazite and xenotime

Most of the monazites found in the polished thin sections were either too small to be analyzed or metamictic with high amounts of common Pb. Successful analyses are presented in Table 5 and on concordia diagrams in Fig. 10. Monazite ages include one Archean ( $2563 \pm 54\ \text{Ma}$ ), two 2.05 Ga domains, and a pooled age of  $1781 \pm 32\ \text{Ma}$  from a monazite in a cross-cutting vein (Fig. 9). Two xenotime grains in sample A2011 give a pooled age of  $1971 \pm 47\ \text{Ma}$ . The large calculated error is partially the result of lead loss together with some isotopic heterogeneity shown by most concordant analyses (c. 1.91 Ga and c. 1.85 Ga; Table 5).

## 5. Discussion

### 5.1. Deposition age and tectonic setting

As was discussed in Section 2.2, we assume that the cratonic sequences in the Koli-Kontiolahti area (Figs. 1 and 2) are dominantly  $>2.1\ \text{Ga}$  in age and that the tectonic setting varies from cratonic aeolian to fluvial. The shallow marine 2.1–2.05 Ga carbonates, mafic volcanic rocks, and mafic pelites, found elsewhere in eastern Finland, which are related to the incipient phase of continental breakup (Kohonen, 1995; Laajoki, 2005), are not found in the Koli-Kontiolahti area. The maximum deposition age of the Hovinvaara lithotype is Archean based on the detrital zircon ages but a c. 2.1–2.05 Ga or even younger deposition age is proposed. The Hovinvaara arkoses are here correlated with the Rekivaara arkoses (A1365), north of the 2.1 Ga Tohmajärvi volcano–plutonic complex (Fig. 1). The Valkeasuo wacke A1364 has a maximum deposition age of 2.04–2.05 Ga. The Archean age population in A2012 has characteristics similar to A1364. Both samples are lacking  $<2.70\ \text{Ga}$  zircons, which are common in LA 1 (A2010) and the Kalliojärvi lithotype (A1159; Appendix 2).

The maximum deposition age for the uppermost stratigraphic part of LA1 is 1.92–1.91 Ga (Fig. 7a). The detrital zircon data indicate a dominant Neoproterozoic source which, based on the well rounded nature of zircon grains, was mainly recycled through the mature quartzites (fluvial–aeolian) from the cratonic sequences. The low Th/Sc and Th/Cr in the LA 1 samples (Fig. 3) indicate elevated mafic component, probably from Archean sedimentary rocks with a komatiite component and Paleoproterozoic mafic rocks (Lahtinen, 2000; Lahtinen et al., 2010). Sample 1A-RLL-08 with  $\varepsilon_{\text{Nd}}$  (1.9) of  $-1.3$  (Table 1) has a major alkaline component derived from a Paleoproterozoic source. One possible source is 2.05 Ga (GTK, unpublished data) volcanic rocks of bimodal alkaline affinity (e.g. Siilinjärvi volcanic complex; Fig. 1). The LA 1 rocks are inferred to represent either collisional early foredeep or backbulge deposits that are deposited during initial basin formation on the lower plate.

The sample A2011 from the Ylemmäinen lithotype has a major Paleoproterozoic detrital zircon component (65%) and a maximum deposition age of c. 1.91 Ga (Fig. 7 and Appendix 2). The deep sea turbidite sequences, including the Kuhnusta assemblage (Fig. 1), also have c. 70% of Paleoproterozoic zircons (Lahtinen et al., 2010). But whereas  $>50\%$  of Paleoproterozoic zircons in the cumulated data, from the rocks correlative with Kuhnusta, are 1.95–2.00 Ga in age, only one zircon out of 28 Paleoproterozoic zircons in the Ylemmäinen sample A2011 plots in this age range. More data are needed but if this is a consistent feature it implies that the source for the Ylemmäinen

**Table 1**

Sm–Nd isotope data and selected element ratios for the Paleoproterozoic metasedimentary cover along the western edge of the Karelian province.

| Sample                               |                            | Type             | Th/<br>Sc | Th/La | Ce/<br>Ce* | National grid<br>coordinates |         | Sm<br>ppm | Nd<br>ppm | <sup>147</sup> Sm/<br><sup>144</sup> Nd | <sup>143</sup> Nd/<br><sup>144</sup> Nd | 2 sigma<br>error | ε <sub>Nd</sub> (1.9) | T <sub>DM</sub><br>Ma | Av. U–Pb<br>age <sup>b</sup><br>TIMS/<br>LA-MCICPMS<br>Ma |
|--------------------------------------|----------------------------|------------------|-----------|-------|------------|------------------------------|---------|-----------|-----------|-----------------------------------------|-----------------------------------------|------------------|-----------------------|-----------------------|-----------------------------------------------------------|
|                                      |                            |                  |           |       |            | x                            | y       |           |           |                                         |                                         |                  |                       |                       |                                                           |
| Foredeep to foreland basin sequences |                            |                  |           |       |            |                              |         |           |           |                                         |                                         |                  |                       |                       |                                                           |
| 1A-RLL-08                            | Psammite                   | LA 1             | 0.59      | 0.23  | 0.98       | 3649827                      | 6980211 | 25.61     | 121.96    | 0.1269                                  | 0.511703                                | 0.000010         | −1.3                  | 2354                  | na/2600                                                   |
| A2010                                | Psammite                   | LA 1             | 0.51      | 0.28  | 0.96       | 3649827                      | 6980211 | 9.16      | 46.11     | 0.1200                                  | 0.511642                                | 0.000010         | −0.8                  | 2279                  |                                                           |
| 4B-RLL-08                            | Pelite                     | LA 1             | 0.38      | 2.25  | 1.52       | 3650024                      | 6980267 | 1.59      | 4.74      | 0.2027                                  | 0.511559                                | 0.000010         | −22.7                 |                       |                                                           |
| 1A-Hauta-08                          | Quartz arenite             | LA 1             | 0.56      | 0.30  | 0.99       | 3650120                      | 6980298 | 1.15      | 6.49      | 0.1078                                  | 0.511272                                | 0.000010         | −5.1                  | 2552                  |                                                           |
| 1B-Hauta-08                          | Pelite                     | LA 1             | 0.46      | 0.49  | 0.96       | 3650120                      | 6980298 | 3.74      | 19.69     | 0.1148                                  | 0.511279                                | 0.000010         | −6.6                  | 2728                  |                                                           |
| 7-RLL-08                             | Pelite                     | LA 1             | 0.50      | 0.97  | 1.80       | 3650114                      | 6980281 | 2.67      | 11.64     | 0.1387                                  | 0.511382                                | 0.000010         | −10.5                 | 3440                  |                                                           |
| 21-JJK-85                            | Pelite                     | LA 1             | 0.32      | 11.90 | 1.89       | 3649322                      | 6979313 | 1.29      | 2.21      | 0.3537                                  | 0.511852                                | 0.000014         | −53.9                 |                       |                                                           |
| S48                                  | Pelite                     | LA 2             | 0.66      | 1.28  | 1.18       | 3630846                      | 7000912 | 2.02      | 8.53      | 0.1431                                  | 0.511437                                | 0.000011         | −10.5                 | 3549                  |                                                           |
| S48B                                 | Pelite                     | LA 2             | 0.43      | 0.83  | 1.04       | 3630846                      | 7000912 | 3.28      | 13.96     | 0.1420                                  | 0.511575                                | 0.000010         | −7.5                  | 3163                  |                                                           |
| S49                                  | Pelite + quartz<br>arenite | LA 1             | 0.59      | 0.78  | 1.51       | 3650115                      | 6980253 | 1.93      | 9.22      | 0.1267                                  | 0.511475                                | 0.000010         | −5.7                  | 2764                  |                                                           |
| S50                                  | Pelite                     | LA 2             | 0.42      | 0.80  | 1.02       | 3630773                      | 7001620 | 2.26      | 9.96      | 0.1374                                  | 0.511522                                | 0.000010         | −7.4                  | 3077                  |                                                           |
| S51A                                 | Pelite                     | LA 1             | 0.34      | 1.34  | 0.98       | 3625429                      | 7009260 | 2.28      | 7.56      | 0.1820                                  | 0.511627                                | 0.000010         | −16.3                 |                       |                                                           |
| S51B                                 | Pelite                     | LA 1             | 0.31      | 1.32  | 1.04       | 3625429                      | 7009260 | 2.19      | 6.99      | 0.1897                                  | 0.511582                                | 0.000010         | −19.0                 |                       |                                                           |
| S51C                                 | Pelite                     | LA 1             | 0.33      | 1.39  | 1.01       | 3625429                      | 7009260 | 1.50      | 5.57      | 0.1632                                  | 0.511538                                | 0.000010         | −13.4                 |                       |                                                           |
| S51D                                 | Pelite                     | LA 1             | 0.36      | 1.55  | 0.88       | 3625429                      | 7009260 | 1.90      | 7.09      | 0.1619                                  | 0.511623                                | 0.000011         | −11.4                 |                       |                                                           |
| 88-JJK-88                            | Pelite                     | LA 3             | 0.38      | 0.31  | 1.00       | 3643581                      | 6979057 | 5.72      | 30.27     | 0.1143                                  | 0.511462                                | 0.000011         | −2.9                  | 2425                  |                                                           |
| 18-RLL-08                            | Psammite                   | Ylemmäinen       | 1.10      | 1.45  | 1.45       | 3648815                      | 6979214 | 2.09      | 8.47      | 0.1494                                  | 0.511640                                | 0.000010         | −8.0                  | 3397                  |                                                           |
| 19-RLL-08                            | Psammite                   | Ylemmäinen       | 0.99      | 2.01  | 1.44       | 3648592                      | 6979293 | 2.07      | 7.41      | 0.1689                                  | 0.511639                                | 0.000010         | −12.8                 | 5332                  |                                                           |
| 20-RLL-08                            | Psammite                   | Ylemmäinen       | 0.65      | 0.42  | 1.01       | 3647890                      | 6979634 | 3.97      | 20.09     | 0.1194                                  | 0.511487                                | 0.000010         | −3.7                  | 2519                  |                                                           |
| 26-RLL-08                            | Psammite                   | Ylemmäinen       | 0.72      | 1.36  | 1.90       | 3646168                      | 6979046 | 2.64      | 8.94      | 0.1785                                  | 0.511664                                | 0.000010         | −14.7                 | 8400                  |                                                           |
| A2011                                | Psammite                   | Ylemmäinen       | 0.53      | 0.15  | 0.87       | 3646168                      | 6979046 | 7.32      | 44.05     | 0.1004                                  | 0.511453                                | 0.000010         | 0.3                   | 2135                  | na/2284                                                   |
| S28/<br>A1159#2 <sup>a</sup>         | Graywacke                  | Kalliojärvi      | 0.55      | 0.32  | 0.93       | 3644652                      | 6977585 | 3.51      | 18.55     | 0.1145                                  | 0.511429                                | 0.000014         | −3.6                  | 2485                  | 2644/2624                                                 |
| Rift related sequences               |                            |                  |           |       |            |                              |         |           |           |                                         |                                         |                  |                       |                       |                                                           |
| S53                                  | Quartzwacke                | Hovinvaara       | 2.28      | 1.03  | 1.15       | 3638426                      | 6984404 | 1.00      | 4.34      | 0.1398                                  | 0.511452                                | 0.000028         | −9.4                  | 3341                  |                                                           |
| A2012                                | Arkose                     | Hovinvaara       | 1.03      | 0.36  | 0.85       | 3638049                      | 6984754 | 2.22      | 13.52     | 0.0993                                  | 0.511064                                | 0.000010         | −7.0                  | 2640                  | na/2767                                                   |
| A1365                                | Arkose                     | Elinaho          | 0.89      | 1.23  | 1.03       | 3658064                      | 6928682 | 1.08      | 4.66      | 0.1399                                  | 0.511232                                | 0.000012         | −13.7                 | 3835                  | 2676/na                                                   |
| A1364 <sup>a</sup>                   | Wacke                      | Valkeasuo        | 0.61      | 0.30  | 0.99       | 3667173                      | 6918840 | 3.23      | 16.69     | 0.1170                                  | 0.511324                                | 0.000010         | −6.3                  | 2721                  | 2646/2743                                                 |
| Cratonic sequences                   |                            |                  |           |       |            |                              |         |           |           |                                         |                                         |                  |                       |                       |                                                           |
| S43                                  | Quartz arenite             | Koli Fm          | 4.35      | 0.68  | 1.33       | 3653067                      | 6983946 | 1.53      | 6.31      | 0.1472                                  | 0.511207                                | 0.000010         | −16.0                 | 4400                  |                                                           |
| S44                                  | Sericite schist            | Jero Fm          | 2.40      | 1.75  | 1.16       | 3649414                      | 6987981 | 1.41      | 4.87      | 0.1751                                  | 0.511430                                | 0.000023         | −18.4                 |                       |                                                           |
| S44#                                 |                            |                  |           |       |            |                              |         | 1.43      | 5.06      | 0.1704                                  | 0.511415                                | 0.000030         | −17.6                 |                       |                                                           |
| S45                                  | Sericite arkose            | Jero Fm          | 2.96      | 0.35  | 0.84       | 3649761                      | 6986125 | 1.70      | 9.55      | 0.1075                                  | 0.511142                                | 0.000010         | −7.5                  | 2738                  |                                                           |
| S47                                  | Sericite schist            | Urkkavaara<br>Fm | 1.99      | 0.64  | 0.98       | 3647173                      | 6970763 | 6.16      | 34.78     | 0.1070                                  | 0.511005                                | 0.000010         | −10.1                 | 2927                  |                                                           |
| 10-RLL-08                            | Conglomerate<br>matrix     | Jero Fm          | 3.37      | 0.93  | 1.17       | 3649460                      | 6979366 | 1.70      | 9.01      | 0.1139                                  | 0.511046                                | 0.000010         | −11.0                 | 3070                  |                                                           |
| 12-RLL-08                            | Conglomerate<br>matrix     | Jero Fm/LA<br>1? | 2.05      | 22.60 | 1.67       | 3649358                      | 6979511 | 0.37      | 0.71      | 0.3202                                  | 0.512104                                | 0.000017         | −40.8                 |                       |                                                           |
| 38-RLL-08                            | Quartz arenite             | Puso Fm          | 2.36      | 0.54  | 1.08       | 3648076                      | 6986324 | 1.43      | 7.27      | 0.1186                                  | 0.511129                                | 0.000018         | −10.5                 | 3199                  |                                                           |

T<sub>DM</sub> calculated according to DePaolo (1981).<sup>a</sup> Reference: 1 – Lahtinen et al., 2010.<sup>b</sup> Average zircon <sup>207</sup>Pb/<sup>206</sup>Pb age; multi grain TIMS (generally discordant)/LA-MCICPMS (na = not analyzed).

lithotype is different from that of the deep water turbidites. Tentatively it is proposed that the source rocks for the Ylemmäinen lithotype are from the plate margin in the present west. Uplift of this source, resulting from continued convergence, resulted in erosion

and high sedimentation rates and deposition of derived material as the foreland basin fills upon early foredeep deposits (LA 1 and LA 3).

The deposition age of Kalliojärvi lithotype turbiditic rocks is difficult to interpret due to a lack of any clear cluster in the ages of the youngest dated grains to clearly define the maximum deposition age. An age about 1.91–1.92 Ga is proposed and younger age domains at ca. 1.88–1.87 Ga are considered to record metamorphic or later hydrothermal events (Fig. 7b). The Archean age population is dominated by <2.75 Ga zircons (78%), similar to LA 1 sample A2010. If the Kalliojärvi turbidites were deposited coevally with the LA 1, they could represent deeper water turbidites of the same foredeep stage. No age data yet exist from LA 3 rocks but a depositional link with LA 1 is favored (Kohonen, 1995).

## 5.2. LREE mineralogy and mobility in the study area

The most common LREE-rich minerals in these samples are monazite and bastnäsite (REE carbonate). Monazite is a common mineral in sedimentary rocks. Monazite dissolution and reprecipitation can

**Table 2**

Rb–Sr isotopic data.

| Sample <sup>a</sup> | Rock type   | Rb<br>(ppm) | Sr<br>(ppm) | <sup>87</sup> Rb/ <sup>86</sup> Sr<br>(±1%) | <sup>87</sup> Sr/ <sup>86</sup> Sr | 2sem    |
|---------------------|-------------|-------------|-------------|---------------------------------------------|------------------------------------|---------|
| S48B                | LA 2 pelite | 188.4       | 185.94      | 2.9606                                      | 0.789362                           | 0.00003 |
| S51B                | LA 1 pelite | 152.56      | 63.02       | 7.1455                                      | 0.893645                           | 0.00003 |
| S51C                | LA 1 pelite | 158.94      | 54.48       | 8.6425                                      | 0.930897                           | 0.00003 |
| S51D                | LA 1 pelite | 136.18      | 91.34       | 4.3710                                      | 0.823856                           | 0.00003 |

Chemical preparation: Tuula Hokkanen.

Rb was measured on Nu MCICPMS using method by Waight et al. (2002); Yann Lahaye.

Sr was measured on VG Sector 54 mass-spectrometer: Arto Pulkkinen.

<sup>87</sup>Sr/<sup>86</sup>Sr ratio is normalized to <sup>86</sup>Sr/<sup>88</sup>Sr = 0.1194.<sup>a</sup> Sample locations in Table 1.

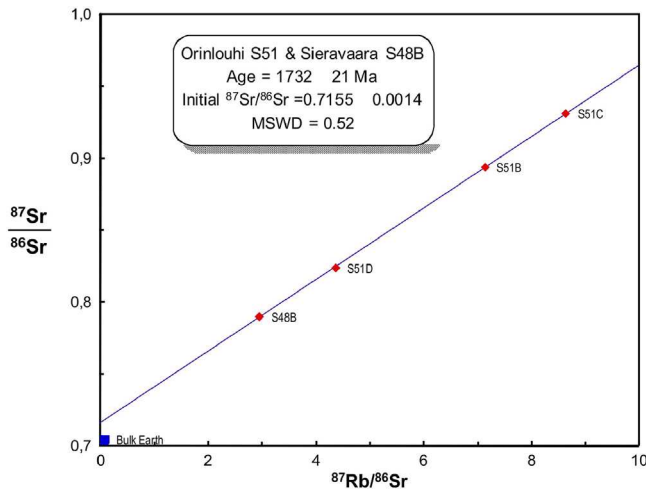


Fig. 5. Rb–Sr isotopic data.

occur already during diagenesis (Bock et al., 2004; Burnotte et al., 1989; Lev et al., 1999; Milodowski and Zalasiewicz, 1991). New monazite growth is common in greenschist- to granulite-facies conditions (Hansen and Harlov, 2007; Kohn and Malloy, 2004; Rasmussen and Muhling, 2009; Rubatto et al., 2001; Schaltegger et al., 1999; Smith and Barreiro, 1990; Tuisku and Huhma, 2006). Based on the late crystallized nature of the monazite crystals (Fig. 9) it seems that most of the monazites post-date the major deformations. Some

Archean detrital monazites are preserved as shielded inclusions in detrital quartz grains (38-RLL-08 in Fig. 9). The c. 2.05 Ga ages could either be from the detrital domain or the result of mixed ages (see grain 1A-Hauta-08 in Table 5).

The young post-tectonic monazites are characterized by low Th (<1.0% ThO<sub>2</sub>) and Pb (<0.1% PbO), which is a characteristic feature for low grade metamorphic or diagenetic monazites (Rasmussen and Muhling, 2009). Low ThO<sub>2</sub> contents below ~<0.1% is a criterion for identifying hydrothermal from igneous monazites, which typically contain 2–12% ThO<sub>2</sub> (Burnotte et al., 1989; Schandl and Gorton, 2004).

Bastnäsite [(Ce, La, Y)CO<sub>3</sub>F] is a mineral rare in subalkaline rocks whereas fairly common in carbonatites and alkaline rocks. There is no evidence from the literature of bastnäsite having been reported from typical siliciclastic sedimentary rocks. It is the only LREE-rich phase in sample 1A-RLL-08 with abundant ilmenite and apatite. This sample has high TiO<sub>2</sub> (2.03%), P<sub>2</sub>O<sub>5</sub> (0.97%), Zr (491 ppm), Nb (33 ppm), and REE (Fig. 4). We infer a major component from the alkaline-affinity volcanic/plutonic rocks, which could also explain the occurrence of F-rich mineral bastnäsite. Berger et al. (2008) noticed that bastnäsite can form at the expense of allanite if the fluid contains H<sub>2</sub>O, CO<sub>2</sub> and F. This could explain the occurrence of bastnäsite in some samples and the rarity of allanite. There are minute crystals of bastnäsite inside detrital minerals but the late- to post-tectonic grains (Fig. 9) also show that bastnäsite has, in most cases, crystallized as new larger grains.

Based on the LREE mineralogy of the non-altered and least altered samples (Th/La ≤ 0.5 in Table 3) it seems that monazite and bastnäsite were the original LREE sources in the LREE depleted samples. Allanite may have also played a role. During the alteration process, monazite was altered to Th-silicates with a variable loss of the LREE (up >95%). Most of the remaining LREE were eventually incorporated in Th-poor monazite. The P-T-X stability of bastnäsite is not well known but probably it easily breaks down releasing LREE. The Th-silicate and xenotime probably incorporated most of the HREE released by monazite dissolution.

The rare earth elements (REE) generally exhibit similar geochemical behavior. Significant exceptions include Ce and Eu, which may occur as multiple valences, i.e. Ce<sup>3+</sup>, Ce<sup>4+</sup> and Eu<sup>2+</sup>, Eu<sup>3+</sup>, in natural environments, allowing for marked fractionation from the other REE. In an oxidizing environment soluble Ce<sup>3+</sup> is oxidized to insoluble Ce<sup>4+</sup> (de Baar et al., 1988; German and Elderfield, 1989). This allows for Ce/Ce\* to be used to infer the conditions of LREE depletion and precipitation. In our case, a positive Ce anomaly is observed in some of the LREE depleted samples (Fig. 4) but mostly Ce has behaved similarly to La and Pr. A positive Ce anomaly characterizes the LREE depleted LA 1 rocks (Fig. 4), which is in accordance with their particularly sulfide-poor nature. It seems that the samples with more than trace sulfide ± graphite generally have only minor or no positive Ce anomaly.

### 5.3. Age constraints for the syn- to post-metamorphic LREE mobility

The maximum deposition age for sample A2011 is 1.91 Ga based on the detrital zircon data (Fig. 7a). Both xenotime and bastnäsite in sample A2011 crystallized after the main deformation event (Fig. 9) during a local peak in metamorphism. The 1917 ± 47 Ma age of xenotime (Fig. 10) dates this event and also gives a minimum age for LREE enrichment (Fig. 4) in this sample. There is a large error in the xenotime age with two nearly concordant ages at c. 1.85 Ga and thus, the metamorphic peak age could be even younger at about 1.87–1.85 Ga. This is indicated by few zircon ages from samples A1159 and A2011, interpreted as hydrothermal/metamorphic in origin. The main tectono-metamorphic stage can thus be bracketed as occurring between 1.91 and 1.85 Ga ago.

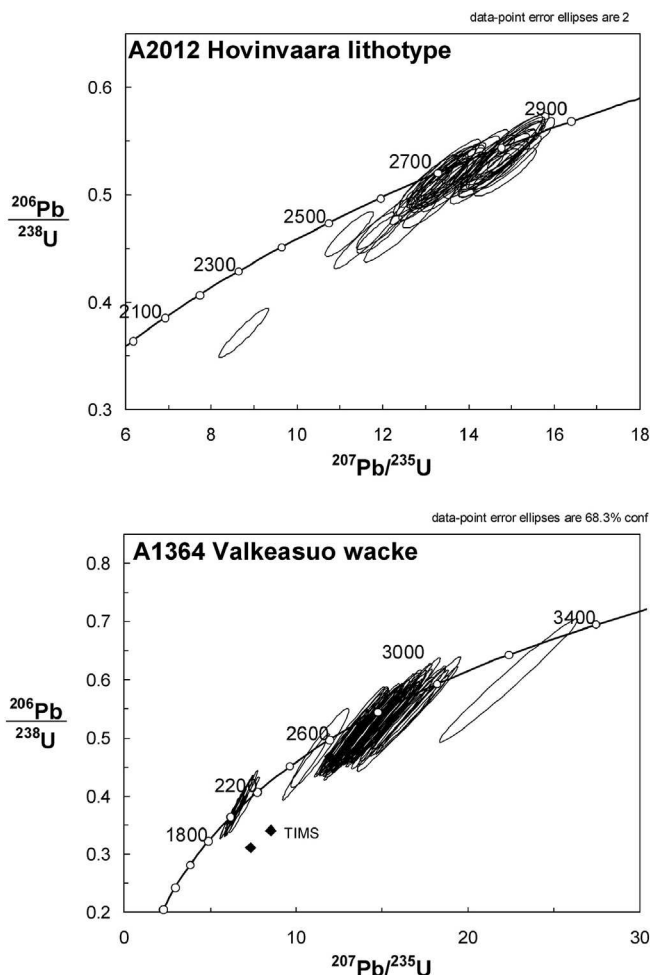
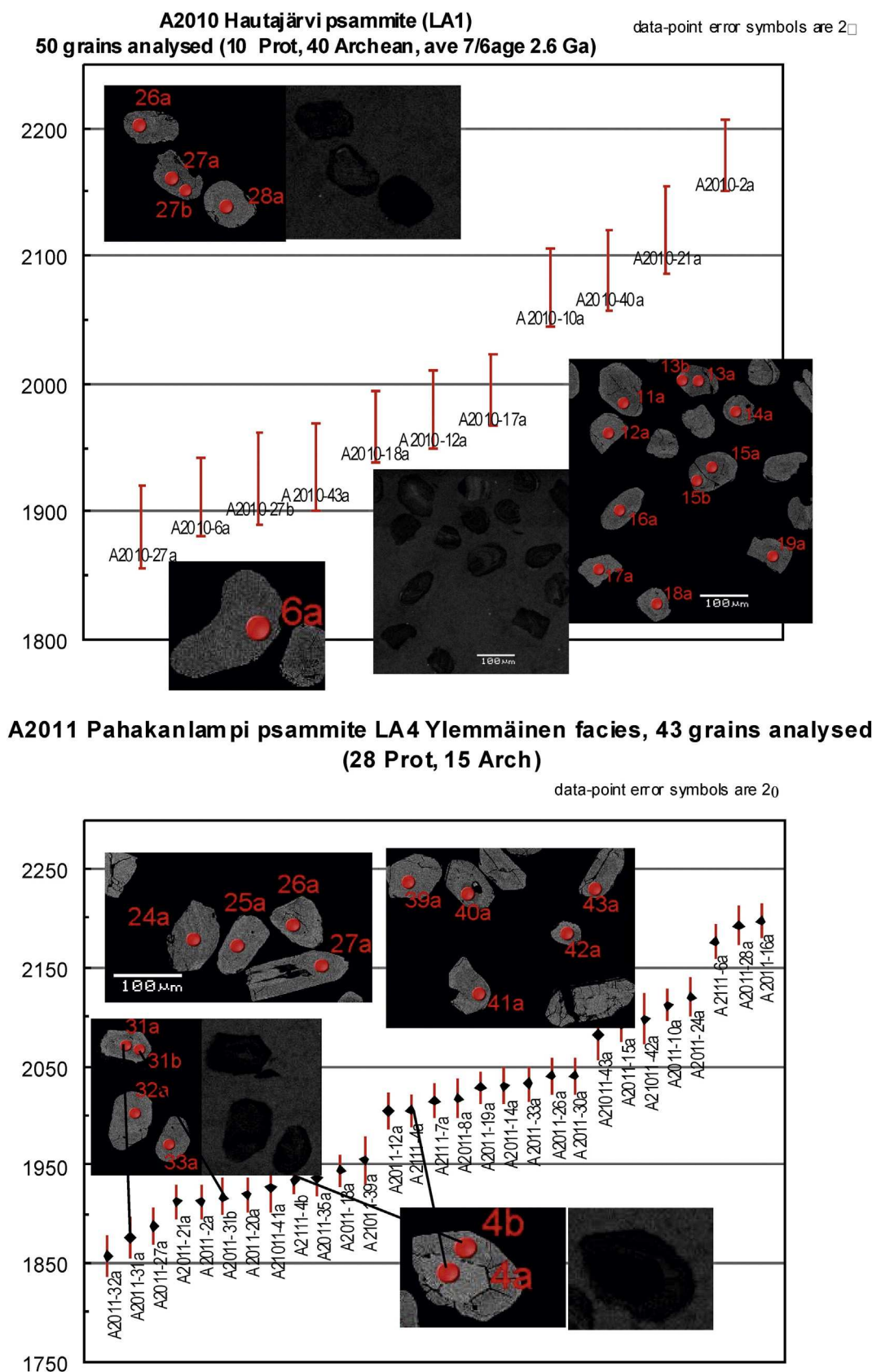


Fig. 6. LA-MC-ICPMS data on samples A2012 and A1364.



The ages of monazite from a thin brittle vein (18-RLL-08) and as a new overgrowth (1A-Hauta-08/1a) over an older grain (Table 5) indicate that one event of monazite crystallization occurred 1.76–1.78 Ga

ago. The Rb–Sr whole rock data suggest that the closure of this isotope system took place  $1732 \pm 21$  Ma (Fig. 5) in the area west of Koli (S51 and S48 in Fig. 1). Smalley et al. (1988) have published a

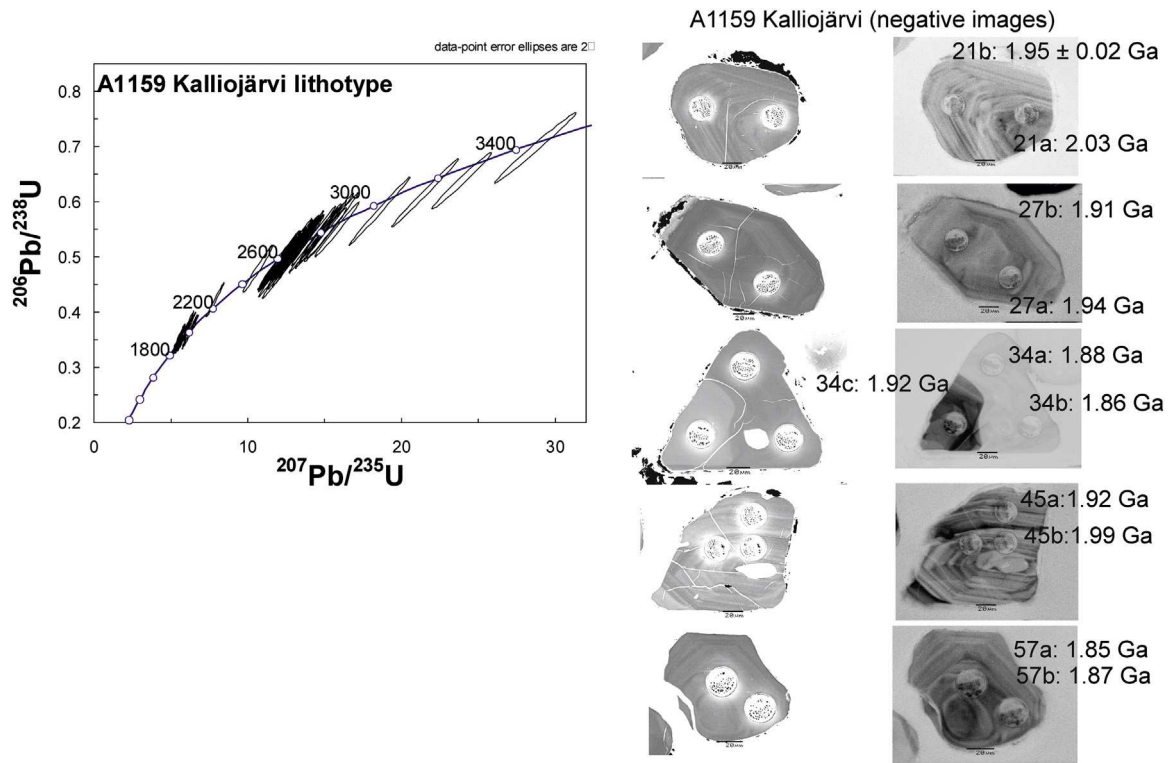


Fig. 8. LA-MC-ICPMS data from sample A1159 with selected CL images of zircons with young ages.

similar whole rock isochron age of  $1729 \pm 40$  Ma for samples west of present study area.

The Sm–Nd results are shown in Fig. 11, which also includes previously published data on cratonic and rift sequences (Huhma, 1987; Lahtinen et al., 2010). The LREE depletion (high Sm/Nd) is obvious in many samples from the LA 1 and Ylemmäinen lithotypes and also in some samples from the cratonic and rift sequences. The Sm–Nd results provide a rough estimate for the timing of the LREE mobility. Samples 26-RLL-08 and A2011, which were taken only 20 cm apart from each other, are chemically identical apart from LREE depletion and enrichment, respectively. The Sm–Nd age of  $412 \pm 27$  Ma from these samples can be considered as the age of the latest LREE depletion (Fig. 11).

Two samples, 21-JJK-85, and 12-RLL-08, which are extremely depleted in LREE also yield Phanerozoic age estimates for depletion. In Fig. 11 the data are also shown in the  $\varepsilon_{\text{Nd}}$  vs. age diagram, where Nd isotope evolution lines are calculated using the measured  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  compositions. Black lines denote the evolution of LA 1 samples, red lines Ylemmäinen samples, and blue line the Kuhnusta assemblage (A1631). Sample S47-Latvajärvi shows Neoproterozoic crustal evolution ( $\varepsilon_{\text{Nd}}(1900) = -10$ ,  $T_{\text{DM}} = 2.93$  Ga). The  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio (0.107) for this sample is most typical for monazite.

Samples 1A-Hauta-08 and 1B-Hauta-08 can be considered as the other end member to account for the minimum age of the latest LREE mobility in typical LA 1 or cratonic sequence samples without any Sm–Nd fractionation. Using the composition of these geochemically similar samples, an age of ca. 360 Ma can be calculated for the depletion in sample 21-JJK-85. Applying pure Archean end member (S47) would indicate that LREE loss took place later ca. 520 Ma ago. Similar estimates for other strongly LREE depleted samples include 0.6–0.8 Ga (conglomerate matrix 12-RLL-08), 0.5–0.9 Ga (4B-RLL-08) and 0.6–1.0 Ga (S51B). There are large uncertainties involved and it is likely that LREE mobilization has occurred in several stages, but fractionation during Phanerozoic time (ca. 0.4 Ga) seems inevitable.

#### 5.4. The probable nature of the altering fluid, element mobility, and the behavior of U

The nature of the altering and LREE carrying fluid is difficult to estimate but the precipitation of new bastnäsite could indicate that the fluid contained  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and F. Positive Ce anomalies in the LREE-depleted samples from the cratonic cover and from LA 1 are consistent with oxidizing conditions in these sulfide-poor rocks. Alkali-bearing, oxidizing, diagenetic brines are possible explanation for the source of the fluid that caused the multi-stage LREE mobility in the study area. González-Álvarez and Kerrich (2010) proposed that possible processes producing alkaline, oxidizing, diagenetic brines in the Belt-Purcell sequence included the enrichment of K in sedimentary rocks, hydrothermal and/or diagenetic alteration of mafic igneous units, and dissolution of evaporitic units. Alkaline material (with bastnäsite) occurs in LA 1 and possibly also in the Ylemmäinen lithotype. Thus, it is possible that bastnäsite-bearing rocks have been present in the source area. A problem with trying to estimate the possible mobility of other elements with that of LREE is the large compositional variation within these rocks. The non-depleted and strongly depleted LA 1 phyllites, with similar HREE level (Fig. 4), show large heterogeneity in their normalized compositions (Fig. 12). Element mobility, i.e., CaO,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , Ba, Rb, and Sr, have most probably occurred in these phyllites. No clear correlation with the LREE depletion is seen. Samples A2011 (enriched in LREE; Fig. 4) and 26-RLL-08 (depleted in LREE), taken 20 cm apart from same unit, have the same chemical composition (Appendix 1). It seems evident that major or minor elements, which despite of their probable variable diagenetic and metamorphic mobility, do not show a clear correlation with LREE depletion. The mobility of U could be at least expected in an oxidized environment. The rocks in the cratonic sequences show very variable Th/U ratios (not shown) indicating both U depletion and enrichment. Otherwise there is little evidence for the mobility of U. The newly precipitated monazites are typically very low in U (Table 4) but this is balanced with high U in the co-precipitated Th-silicates.

**Table 3**  
REE- and Th-rich minerals in sample thin sections scanned for REE minerals.

| Sample      |                     | Type         | Th/La | REE- and Th- rich minerals                                                                                           |
|-------------|---------------------|--------------|-------|----------------------------------------------------------------------------------------------------------------------|
| 1A-Hauta-08 | Quartzite           | LA 1         | 0.30  | Allanite, monazite (ThO <sub>2</sub> 0.0–1.0% and UO <sub>2</sub> 0.0–0.2%; grain 1a in Table 4)                     |
| 1B-Hauta-08 | Pelite              | LA 1         | 0.49  | Monazite (ThO <sub>2</sub> 0.8–4.3% and UO <sub>2</sub> 0.0–0.2%)                                                    |
| 1A-RLL-08   | Psammite            | LA 1         | 0.23  | Bastnäsite (high Y 4.0–7.0%)                                                                                         |
| 4B-RLL-08   | Pelite              | LA 1         | 2.25  | Th-silicate                                                                                                          |
| 7-RLL-08    | Pelite              | LA 1         | 0.97  | Monazite (ThO <sub>2</sub> 0.3–5.0%; grain 1 in Table 4)                                                             |
| 21-JJK-85   | Pelite              | LA 1         | 11.90 | Monazite (ThO <sub>2</sub> 2.6–3.1% and UO <sub>2</sub> 0.0–0.3%), bastnäsite (Y 0.5–1.0%), Th-silicate              |
| 10-RLL-08   | Conglomerate matrix | Jero Fm      | 0.93  | Th-silicate, 1 monazite (ThO <sub>2</sub> 12.0% and UO <sub>2</sub> 0.4%) grain as inclusion in quartz clast         |
| 12-RLL-08   | Conglomerate matrix | Jero Fm/LA 1 | 22.60 | Monazite (ThO <sub>2</sub> 2.5% and UO <sub>2</sub> 0.1–0.3%)                                                        |
| 18-RLL-08   | Psammite            | Ylemmäinen   | 1.45  | 1 monazite (Table 4) grain in 70 µm vein                                                                             |
| 19-RLL-08   | Psammite            | Ylemmäinen   | 2.01  | 1 monazite grain (Table 4)                                                                                           |
| 20-RLL-08   | Psammite            | Ylemmäinen   | 0.42  | Monazite (ThO <sub>2</sub> 3.8–4.5% and UO <sub>2</sub> 0.1–0.2%), xenotime, apatite                                 |
| 26-RLL-08   | Psammite            | Ylemmäinen   | 1.36  | Bastnäsite (Y 0.2–0.5%), Th-silicate, xenotime                                                                       |
| 35-RLL-08   | Arkose              | Hovinvaara   | 1.07  | Monazite (ThO <sub>2</sub> 3.8–5.9% and UO <sub>2</sub> 0.1–0.3%)                                                    |
| 38-RLL-08   | Quartz arenite      | Puso Fm      | 0.54  | Monazite (ThO <sub>2</sub> 7.6–11.1% and UO <sub>2</sub> 0.1–1.2%); one grain (Table 4) as inclusion in quartz clast |
| A2010       | Psammite            | LA 1         | 0.28  | Unspecified Ce-rich oxide (<10 µm)                                                                                   |
| A2011.1     | Psammite            | Ylemmäinen   | 0.15  | Bastnäsite (Y 0.2–4.2%), xenotime, Th-silicate, apatite                                                              |
| A2011.2     |                     |              |       | No REE minerals                                                                                                      |
| A2011.3     |                     |              |       | Small amount of unspecified Th oxide                                                                                 |
| A2012       | Arkose              | Hovinvaara   | 0.36  | Th-silicate                                                                                                          |

Hydrothermal alteration of monazite in the crystalline basement of the Athabasca Basin produced Th-silicates with low U ( $\ll 1\%$  U; Hecht and Cuney, 2000). Similarly low values are not seen in our samples. Uranium mobility in the cratonic cover is recorded in several minor U occurrences in the area (Fig. 1).

#### 5.5. An evolution model for the multi-phased LREE element mobility

The lithostratigraphy and map pattern of the cover sequences in the Koli-Kontiolahti area are rather well constrained (Kohonen and Marmo, 1992) but the boundaries between the units distinguished within the area to the west (Fig. 2) are less well defined and, for the most part, not exposed (Kohonen, 1995). The east-vergent asymmetric folding, characterizing the area, has probably also included thrust faults. The original boundary between LA 1 and the cover is inferred as a depositional interface although it is now tectonized and faulted, probably in several stages. The LA 1 and LA 3 are tentatively considered as time-equivalent units (Kohonen, 1995) and the Ylemmäinen lithotype represents a younger sequence. The Kalliojärvi lithotype is possibly a deeper water time equivalent of LA 1 and LA 3.

There are many unknown aspects in the geological evolution of the study area which makes interpretation of tectonic and basin

evolution difficult. In that light, we propose here a conceptual evolution model to be tested in future studies. Between 2.3–2.1 Ga fluvial to shallow water marine (platformal) conditions prevailed followed by the formation of an incipient 2.1 Ga intracratonic rift basin with tholeiitic volcanism (T in Fig. 1; Ward, 1988). A rift-related crustal-scale marginal fault (Fig. 1) developed and this fault has acted as an important element in later tectonic evolution. Diagenetic reactions start soon after deposition and the basinal oxidizing proto brines started to evolve already at 2.3–2.1 Ga. Deposition of carbonates, black shales, turbidites and pelites, tuffs, and alkaline volcanic complexes occurred along the western margin of the Karelia craton at c. 2.05 Ga and is related to the opening of an ocean. During 2.05–1.92 Ga the Koli-Kontiolahti area is assumed to have been part of a marginal basin close to a non-extended craton margin in the west with the actual plate margin much farther in the west than the present western margin of the Karelia Province. During the initial stage of the continent–arc/continent collision between the Archean craton and a Paleoproterozoic microcontinent–arc collage at c. 1.91–1.90 Ga, a peripheral bulge formed and large parts of the marginal basin were uplifted and eroded. On a tilting erosional substratum a large-scale angular unconformity formed, ultimately exposing the basement south of the study area (Fig. 1). The peripheral bulge then moved farther off to the west and shallow water foredeep deposition

**Table 4**  
Selected monazite, bastnäsite, Th-silicate and xenotime analyses of sedimentary rocks.

| Mineral                                   | Monazite    |           |           |           |           |           | Bastnäsite |           |       | Th-silicate |           |           | Xenotime  |       |
|-------------------------------------------|-------------|-----------|-----------|-----------|-----------|-----------|------------|-----------|-------|-------------|-----------|-----------|-----------|-------|
| Sample                                    | 1A-Hauta-08 | 7-RLL-08  | 18-RLL-08 | 19-RLL-08 | 35-RLL-08 | 38-RLL-08 | 1A-RLL-08  | 26-RLL-08 | A2011 | 4B-RLL-08   | 10-RLL-08 | 26-RLL-08 | 20-RLL-08 | A2011 |
| Grain/<br>points <sup>a</sup>             | 1a/2        | 1/1       | 1/3       | 1/4       | 1/1       | 1/2       | 1/1        | 1/1       | 1/5   | 1/1         | 1/1       | 1/1       | 1/1       | 1/7   |
| La <sub>2</sub> O <sub>3</sub><br>(wt. %) | 15.80       | 13.10     | 13.28     | 12.83     | 16.49     | 9.28      | 11.87      | 14.62     | 15.81 | 0.16        | 0.06      | 0.09      | 0.12      | 0.00  |
| Ce <sub>2</sub> O <sub>3</sub>            | 33.01       | 33.30     | 32.68     | 32.11     | 35.14     | 24.80     | 30.65      | 37.24     | 31.85 | 1.72        | 2.92      | 1.27      | 0.44      | 0.08  |
| Nd <sub>2</sub> O <sub>3</sub>            | 12.15       | 10.35     | 12.93     | 11.38     | 8.97      | 8.92      | 13.60      | 13.56     | 11.78 | 1.24        | 1.23      | 0.41      | 0.00      | 0.00  |
| Y <sub>2</sub> O <sub>3</sub>             | 1.01        | 0.88      | 2.62      | 0.10      | 0.80      | 2.59      | 5.87       | 0.38      | 1.26  | 4.37        | 7.42      | 7.02      | 41.72     | 41.93 |
| P <sub>2</sub> O <sub>5</sub>             | 28.91       | 28.71     | 27.88     | 27.63     | 28.81     | 27.73     | 0.00       | 0.15      | 0.29  | 2.95        | 4.48      | 1.98      | 29.20     | 34.02 |
| PbO                                       | 0.04        | 0.24      | 0.00      | 0.17      | 0.37      | 1.46      | 0.21       | 0.00      | 0.00  | 0.00        | 0.00      | 0.00      | 0.46      | 0.40  |
| ThO <sub>2</sub>                          | 0.09        | 1.78      | 0.36      | 5.07      | 5.92      | 10.82     | 0.31       | 0.96      | 1.60  | 33.18       | 48.17     | 51.44     | 0.24      | 0.21  |
| UO <sub>2</sub>                           | 0.09        | 0.00      | 0.00      | 0.11      | 0.27      | 0.92      | 0.00       | 0.00      | 0.06  | 7.21        | 1.63      | 3.37      | 0.62      | 0.41  |
| CaO                                       | 0.05        | 0.70      | 0.17      | 0.56      | 0.65      | 2.29      | 2.28       | 2.34      | 3.26  | 0.89        | 0.36      | 0.14      | 0.14      | 0.02  |
| SiO <sub>2</sub>                          | 0.45        | 0.80      | 0.35      | 0.84      | 0.82      | 0.92      | 2.67       | 2.70      | 1.92  | 19.45       | 14.19     | 17.24     | 0.82      | 0.68  |
| F                                         | 0.66        | 0.72      | 0.54      | 0.64      | 0.76      | 0.64      | 3.52       | 3.46      | 4.47  | 0.47        | 0.22      | 0.53      | 0.19      | 0.07  |
| Total                                     | 99.13       | 98.13     | 98.95     | 97.89     | 100.39    | 96.58     | 75.98      | 77.35     | 81.96 | 90.81       | 85.21     | 91.93     | 80.68     | 94.89 |
| Age<br>(Ma)                               | 1764 ± 30   | 2034 ± 34 | 1781 ± 32 |           |           | 2561 ± 54 |            |           |       |             |           |           |           |       |

<sup>a</sup> Grain number referred in text and Table 5, Points are the number of analyses either from one grain domain or grain.

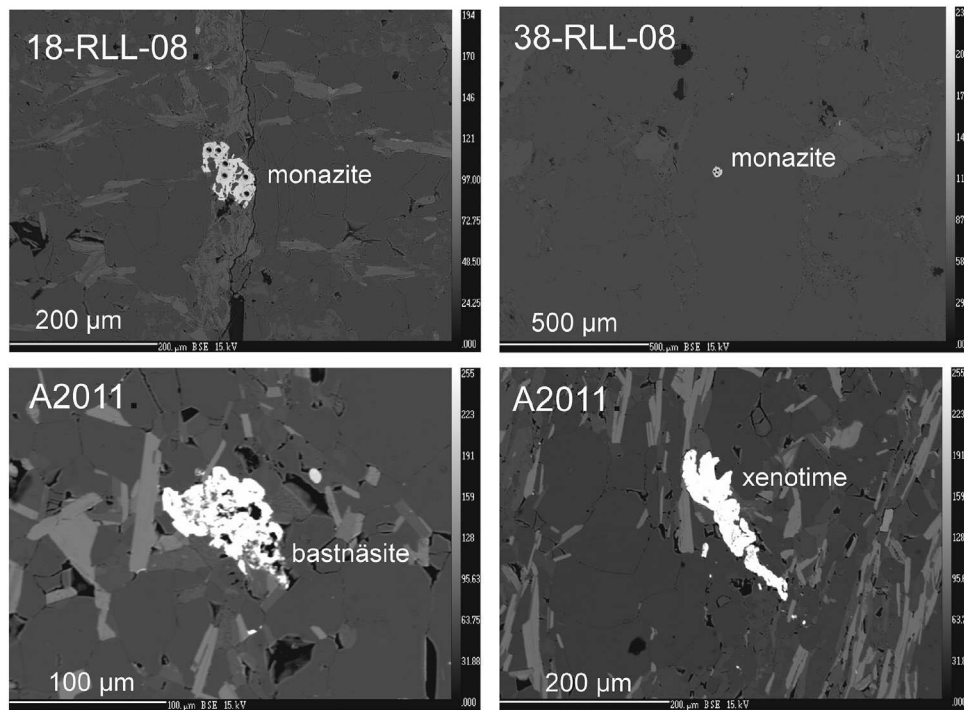


Fig. 9. BSE images of selected REE-bearing phases.

from cratonic, mainly cover, sources occurred (LA 1 and LA 3). At this stage the peripheral bulge prevented material from west of it to be deposited in the study area.

Continued convergence caused the uplift of the earliest fold and thrust units, composed of material from the plate margin sedimentary

and magmatic rocks. Voluminous foreland deposition from the west occurred as exemplified by the Ylemmäinen lithotype rocks. In the newly-formed foredeep to foreland basin, alkaline oxidizing diagenetic brines started to circulate. These fluids were derived from below, from the coarse-grained and porous cratonic and rift-related sequences but

**Table 5**  
U–Pb isotopic data on monazites and xenotimes.

| Sample                        | ppm  | Measured ratios   |                                         |                                         |                                      |         |                                        |      |                                        |        |        | Discordance    | Ages                    |      |                         |      |                         |      |
|-------------------------------|------|-------------------|-----------------------------------------|-----------------------------------------|--------------------------------------|---------|----------------------------------------|------|----------------------------------------|--------|--------|----------------|-------------------------|------|-------------------------|------|-------------------------|------|
|                               | U    | <sup>206</sup> Pb | <sup>206</sup> Pb/ <sub>c</sub><br>(%)* | <sup>206</sup> Pb/<br><sup>204</sup> Pb | <sup>207</sup> Pb/ <sup>206</sup> Pb | 1σ**    | <sup>207</sup> Pb/<br><sup>235</sup> U | 1σ** | <sup>206</sup> Pb/<br><sup>238</sup> U | 1σ**   | Rho*** | Central<br>(%) | <sup>207</sup> /<br>206 | 1σ** | <sup>207</sup> /<br>235 | 1σ** | <sup>206</sup> /<br>238 | 1σ** |
| Monazite one grain per sample |      |                   |                                         |                                         |                                      |         |                                        |      |                                        |        |        |                |                         |      |                         |      |                         |      |
| 7-RLL-08                      | 442  | 541               | 5.30                                    | 245                                     | 0.12535                              | 0.00247 | 6.07                                   | 0.36 | 0.3510                                 | 0.0199 | 0.95   | −5.4           | 2034                    | 34   | 1985                    | 52   | 1939                    | 95   |
| 1A-Hauta-08/1a                | 272  | 297               | 0.00                                    | 6419                                    | 0.10786                              | 0.00185 | 4.86                                   | 0.25 | 0.3271                                 | 0.0155 | 0.94   | 4.0            | 1764                    | 30   | 1796                    | 42   | 1824                    | 75   |
| 1A-Hauta-08/1b                | 51.0 | 66.1              | 0.00                                    | 1005                                    | 0.12901                              | 0.00299 | 6.90                                   | 0.41 | 0.3881                                 | 0.0210 | 0.92   | 1.7            | 2084                    | 38   | 2099                    | 52   | 2114                    | 97   |
| 20-RLL-08                     | 535  | 315               | 11.00                                   | 120                                     | 0.09803                              | 0.00211 | 2.20                                   | 0.11 | 0.1624                                 | 0.0071 | 0.90   | −41.8          | 1587                    | 39   | 1180                    | 34   | 970                     | 39   |
| 38-RLL-08                     | 6311 | 11375             | 0.18                                    | 7538                                    | 0.16726                              | 0.00266 | 10.42                                  | 0.51 | 0.4518                                 | 0.0208 | 0.95   | −6.0           | 2530                    | 27   | 2473                    | 45   | 2403                    | 92   |
| 38-RLL-08                     | 6807 | 12399             | 0.02                                    | 76415                                   | 0.17371                              | 0.00214 | 11.27                                  | 0.63 | 0.4707                                 | 0.0258 | 0.98   | −5.0           | 2594                    | 21   | 2546                    | 52   | 2487                    | 113  |
| 38-RLL-08                     | 108  | 208               | 0.00                                    | 2542                                    | 0.17314                              | 0.00535 | 11.40                                  | 0.66 | 0.4774                                 | 0.0236 | 0.85   | −3.4           | 2588                    | 49   | 2556                    | 54   | 2516                    | 103  |
| 18-RLL-08                     | 71.0 | 86.0              | 1.40                                    | 922                                     | 0.11266                              | 0.00293 | 4.89                                   | 0.24 | 0.3147                                 | 0.0129 | 0.85   | −4.9           | 1843                    | 48   | 1800                    | 41   | 1764                    | 63   |
| 18-RLL-08                     | 67.0 | 74.9              | 1.10                                    | 506                                     | 0.10774                              | 0.00184 | 4.48                                   | 0.21 | 0.3014                                 | 0.0131 | 0.93   | −4.1           | 1762                    | 31   | 1727                    | 39   | 1698                    | 65   |
| 18-RLL-08                     | 124  | 142               | 0.00                                    | 2578                                    | 0.11023                              | 0.00152 | 4.65                                   | 0.21 | 0.3059                                 | 0.0129 | 0.95   | −5.2           | 1803                    | 24   | 1758                    | 37   | 1720                    | 64   |
| A2011 xenotime grain 1        |      |                   |                                         |                                         |                                      |         |                                        |      |                                        |        |        |                |                         |      |                         |      |                         |      |
| A2011                         | 1054 | 3492              | 0.19                                    | 16903                                   | 0.11379                              | 0.00080 | 4.86                                   | 0.08 | 0.3099                                 | 0.0045 | 0.90   | −7.4           | 1861                    | 12   | 1796                    | 13   | 1740                    | 22   |
| A2011                         | 925  | 3306              | 0.51                                    | 8656                                    | 0.11271                              | 0.00077 | 5.29                                   | 0.16 | 0.3405                                 | 0.0101 | 0.97   | 2.8            | 1844                    | 12   | 1868                    | 26   | 1889                    | 48   |
| A2011                         | 984  | 3434              | 0.00                                    | 24252                                   | 0.11695                              | 0.00078 | 5.34                                   | 0.11 | 0.3309                                 | 0.0064 | 0.95   | −4.0           | 1910                    | 11   | 1875                    | 17   | 1843                    | 31   |
| A2011                         | 1086 | 3667              | 0.00                                    | 20423                                   | 0.11746                              | 0.00083 | 5.19                                   | 0.08 | 0.3206                                 | 0.0045 | 0.89   | −7.5           | 1918                    | 12   | 1851                    | 13   | 1793                    | 22   |
| A2011                         | 721  | 2448              | 0.22                                    | 8883                                    | 0.11328                              | 0.00094 | 5.09                                   | 0.14 | 0.3257                                 | 0.0084 | 0.95   | −2.2           | 1853                    | 15   | 1834                    | 23   | 1817                    | 41   |
| A2011                         | 506  | 1546              | 0.00                                    | 6822                                    | 0.11401                              | 0.00126 | 4.52                                   | 0.12 | 0.2876                                 | 0.0066 | 0.90   | −14.2          | 1864                    | 18   | 1735                    | 21   | 1630                    | 33   |
| A2011                         | 889  | 2934              | 0.00                                    | 22110                                   | 0.11562                              | 0.00095 | 4.94                                   | 0.09 | 0.3098                                 | 0.0049 | 0.89   | −9.0           | 1890                    | 13   | 1809                    | 15   | 1740                    | 24   |
| A2011                         | 451  | 1526              | 0.02                                    | 7065                                    | 0.11403                              | 0.00098 | 4.94                                   | 0.10 | 0.3144                                 | 0.0056 | 0.90   | −6.3           | 1865                    | 15   | 1810                    | 17   | 1762                    | 27   |
| A2011                         | 830  | 2522              | 0.91                                    | 1815                                    | 0.11233                              | 0.00142 | 4.47                                   | 0.14 | 0.2885                                 | 0.0083 | 0.92   | −12.5          | 1837                    | 22   | 1725                    | 26   | 1634                    | 42   |
| A2011                         | 705  | 1981              | 0.70                                    | 914                                     | 0.11038                              | 0.00096 | 4.06                                   | 0.15 | 0.2667                                 | 0.0093 | 0.97   | −17.5          | 1806                    | 16   | 1646                    | 29   | 1524                    | 47   |
| A2011 xenotime grain 2        |      |                   |                                         |                                         |                                      |         |                                        |      |                                        |        |        |                |                         |      |                         |      |                         |      |
| A2011                         | 139  | 441               | 0.54                                    | 3394                                    | 0.11413                              | 0.00168 | 4.49                                   | 0.21 | 0.2856                                 | 0.0129 | 0.95   | −14.9          | 1866                    | 25   | 1730                    | 39   | 1619                    | 65   |
| A2011                         | 1444 | 4359              | 0.64                                    | 1941                                    | 0.11196                              | 0.00127 | 4.37                                   | 0.11 | 0.2834                                 | 0.0063 | 0.89   | −13.8          | 1831                    | 19   | 1707                    | 21   | 1608                    | 32   |
| A2011                         | 699  | 2195              | 0.07                                    | 12615                                   | 0.11289                              | 0.00125 | 4.58                                   | 0.12 | 0.2945                                 | 0.0069 | 0.90   | −11.2          | 1846                    | 19   | 1746                    | 21   | 1664                    | 34   |
| A2011                         | 881  | 2568              | 0.46                                    | 6553                                    | 0.11194                              | 0.00136 | 4.31                                   | 0.14 | 0.2790                                 | 0.0085 | 0.93   | −15.1          | 1831                    | 22   | 1695                    | 27   | 1586                    | 43   |

<sup>\*</sup>  $^{206}\text{Pb}(\%)$ : percentage of common  $^{206}\text{Pb}$  in measured  $^{206}\text{Pb}$  calculated from the  $^{204}\text{Pb}$  signal using age-related common lead after model by Stacey and Kramers (1975).

<sup>\*\*</sup> Errors are 1-sigma absolute.

<sup>\*\*\*</sup> Rho: Correlation of Pb/U errors.

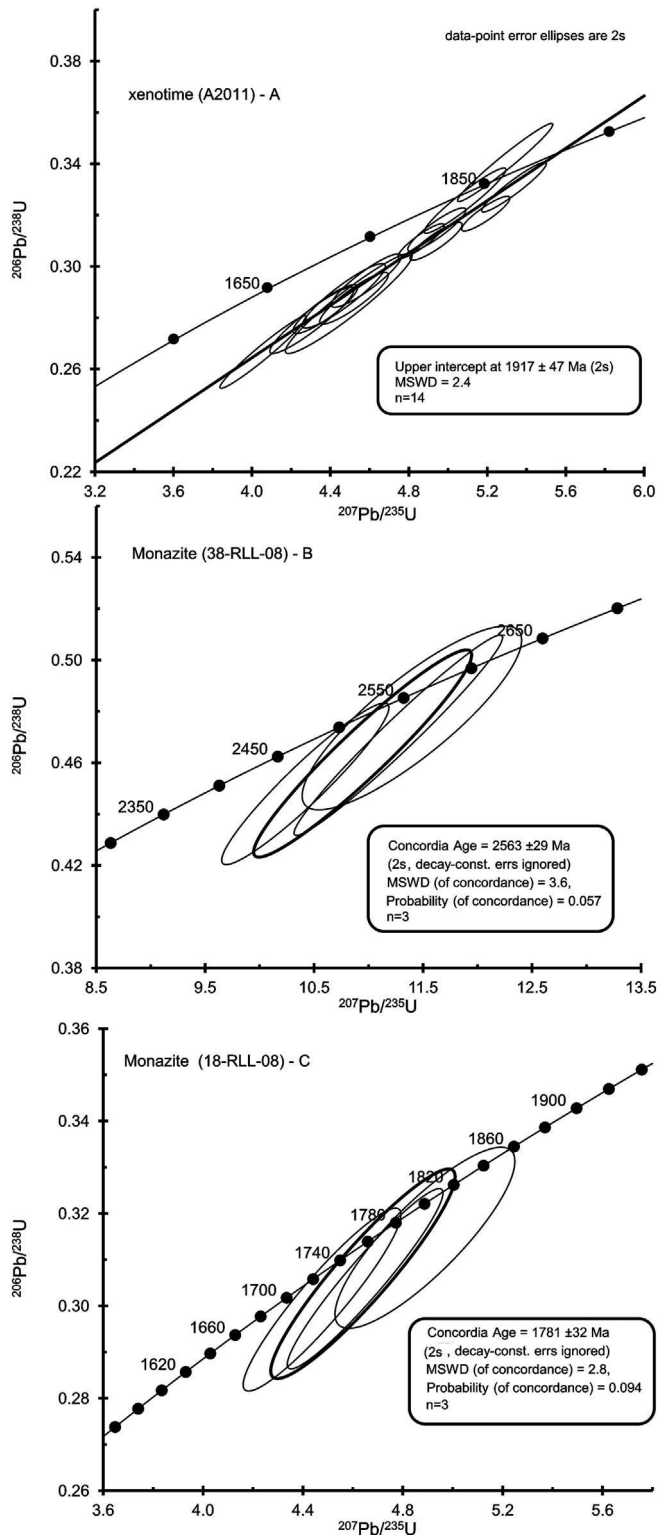


Fig. 10. Concordia diagrams for the LA-MC-ICPMS analyses on xenotime from sample A2011 (A), and monazites from the samples 38-RLL-08 (B), and 18-RLL-08 (C).

became intensified in alkalinity by interaction with the alkaline source component (bastnäsite) in the foredeep to foreland basin sedimentary rocks. Kohonen (1995) interpreted structural evolution in the study area as progressive in nature with an E- to NE-migrating fold and thrust belt gradually rotating to a sinistral transpressive deformation zone. The maximum deposition age of the foredeep to foreland basin is 1.91–1.92 Ga based on detrital zircon data. Using the younger age

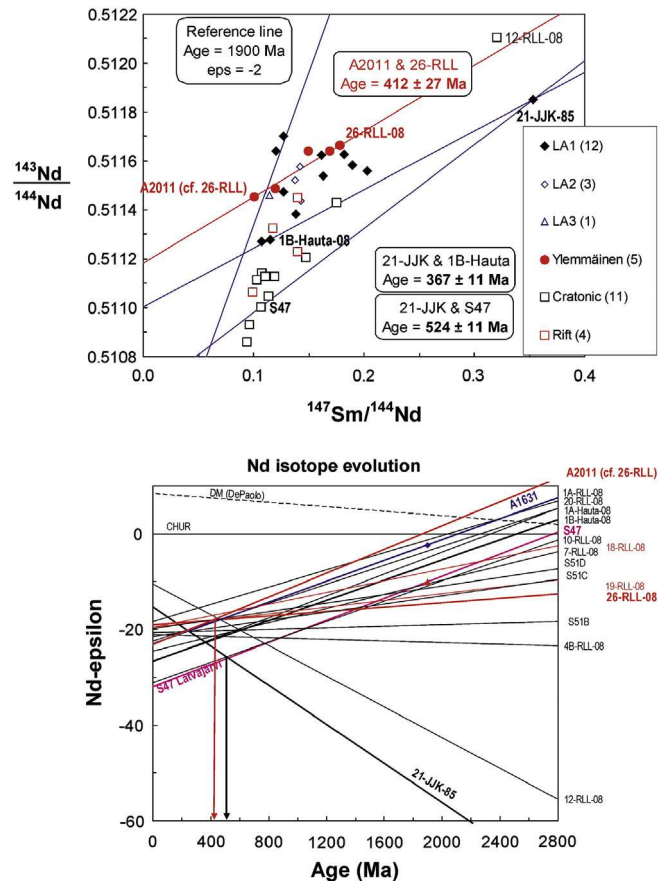


Fig. 11. Sm–Nd isotope diagram showing data from this study, together with some analyses from Huhma (1987) and Lahtinen et al. (2010). Two-point age-calculations are shown for selected samples. The number of samples in each group is given in parentheses. The epsilon vs. age diagram showing evolution lines for selected samples (black – LA1, red – Ylemmäinen lithotype, A1631 Kuhnusta–typical upper Kalevian metasediment, S47 Latvajärvi–Urkkavaara Fm metasediment, typical example of Archean LREE enriched material). The arrows point to the ages of possible REE fractionation between 21-JJK-85 and S47 (black arrow) and A2011 and 26-RLL-08 (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

limit of the heterogeneous xenotime age data and the ages of a few probable metamorphic zircons, the minimum age of peak metamorphism could be at about 1.87–1.86 Ga. The xenotime is from a LREE enriched sample and coeval with bastnäsite. It also gives the minimum age for LREE mobility in this sample. The main tectono-metamorphic stage in the study area can then be bracketed between 1.91 and 1.87–1.86 Ga, which is also one of the episodes when LREE mobility occurred in the whole sedimentary package. With the progression of metamorphic temperature and decrease in porosity it is possible that large amounts of brines became expelled and confined into the fault zones and more porous coarse-grained units. Metamorphic recrystallization reduced the porosity significantly, and thus inhibited pervasive fluid flow after 1.89–1.87 Ga, especially in the fine-grained, clay-rich rocks.

The age of the late sinistral shearing is unknown but, based on the monazite ages (Table 5), it seems that all ductile deformation preceded 1.78–1.76 Ga in these units. The Rb–Sr whole rock closure age  $1732 \pm 21$  Ma (this study) is from samples (S48 and S51B/C/D in Fig. 1) close to a long-lived major fault zone where the marginal fault and the Romppala fault zone coincide. The Sm–Nd age of  $412 \pm 27$  Ma can be considered as the age of latest depletion of LREE in the Ylemmäinen lithofacies. Similar Phanerozoic age estimates for LREE depletion are derived from extremely strongly depleted samples along the contact between the cratonic rocks and LA1. Other strongly LREE depleted samples give similar estimates for depletion at 0.4–1.0 Ga.

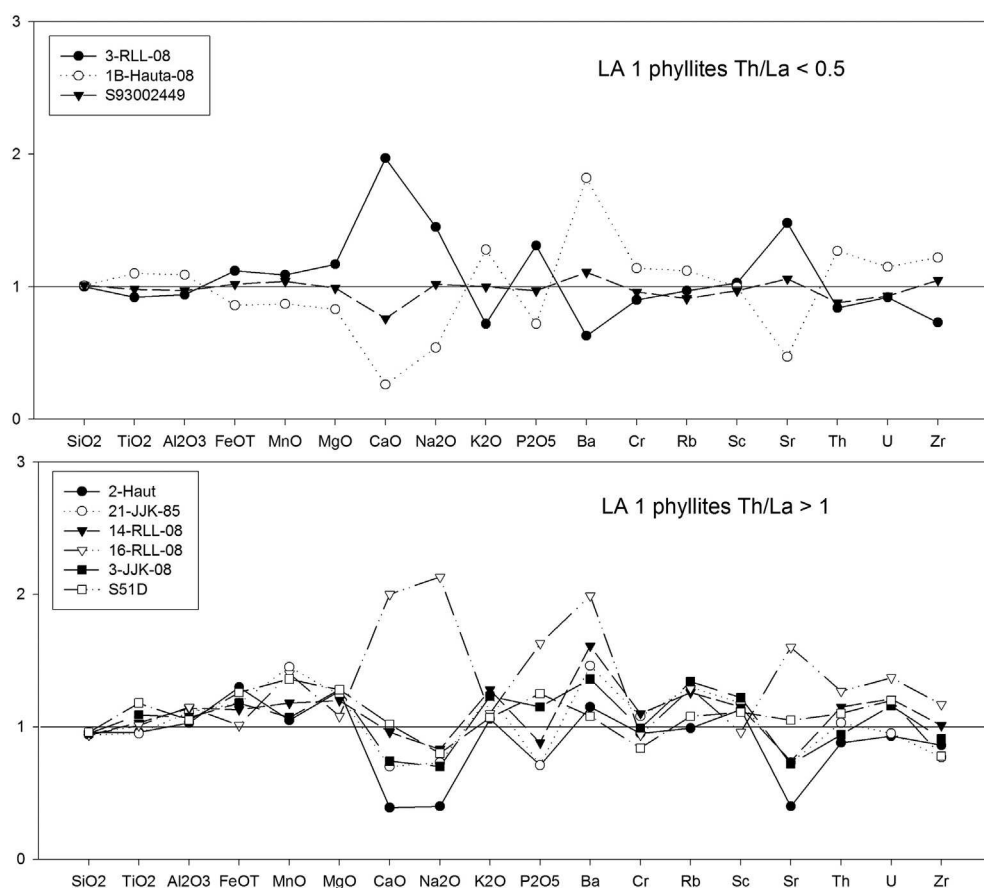


**Fig. 12.** Normalized compositions of selected LA 1 phyllites. Normalization has been carried out with respect to the average composition of non-depleted LA 1 phyllites with non-anomalous HREE (3-RLL-08, 1B-Hauta-08, S93002449; see Fig. 4).

Although the c. 1.78–1.73 Ga and 0.4 Ga LREE mobility events are well constrained, there could also have been mobility events in the time period in between. The Rapakivi event in Salmi, Russia (1.58–1.47 Ga; Koistinen et al., 2001) occurs along the tectonic trend of the 2.1 Ga rift-related marginal fault zone. Many boulders of unmetamorphosed sedimentary rocks have been found in the study area, or along its periphery, indicating that some remnants of yet an undiscovered young sedimentary basin or basins could be hiding under the glaciogenic cover or at the bottoms of natural depressions (lakes). Possible sources for these boulders are the  $\geq 1.3$  Ga intracratonic rift basin and foreland basin related to the Sveconorwegian orogeny (1.1–0.9 Ga) (Kohonen and Rämö, 2005).

Phanerozoic (c. 0.4 Ga) ages have been observed from uraninites (Vaasjoki et al., 2002), fluorite–calcite–galena veins (Alm et al., 2005), and fracture fillings (Sandström and Tullborg, 2009) from different parts of the Fennoscandian Shield. Thus, the 0.4 Ga stage is best explained by the occurrence of a shield-scale foreland basin related to the Caledonian orogenic front (Kohonen and Rämö, 2005) causing heat distribution and fluid circulation. In all of the above cases, the possible 0.4 Ga basin-related imprint on crystalline bedrock occurs in fault and fracture zones, and possibly in microfracture networks. Most of the LREE depletions, with an assumed  $< 1.7$  Ga age in the study area, occur in fault or fracture zones or close to them. The main exception to this is the LREE depletion in some of the Ylemmäinen lithotype samples where it seems to be a surface phenomenon. At least two possibilities exist to interpret the 0.4 Ga LREE depletion in the Ylemmäinen samples. These include alkali-bearing fluid circulation with depth penetration, which has occurred along microfracture networks using limited porosity still left in these rocks or that LREE depletion took place close to the interface of young, un lithified sedimentary rocks with a basal brine aquifer and the immediate underlying crystalline Ylemmäinen rocks.

In our model, alkali-bearing oxidizing fluids started to form maybe as early as 2.3–2.1 Ga ago followed by episodic and protracted fluid migration at least until 0.4 Ga ago (cf. Alexandre et al., 2009; González-Álvarez et al., 2006; Rasmussen et al., 2007). During the younger events fluid migration was focused along fracture zones coupled with the preservation of some broader hydraulic conductivity by means of reactivated microfracture networks (Mercadier et al., 2010). In the metamorphosed coarse-grained sandstone units, such reactivation probably still occurred at 0.4 Ga. A crucial tectonic element was the 2.1 Ga rift related, marginal fault, that steered basin evolution, long-lived faulting, and fluid circulation.

## 6. Conclusions

The Koli-Kontiolahti area records 2.3–2.1 Ga cratonic sedimentation followed by basin evolution with a 2.1–2.05 Ga rift basin and c. 1.91–1.92 foredeep to foreland basin, and inferred basin stages (not preserved in the rock record) at 1.5 Ga (rift basin?),  $\geq 1.3$  Ga (intracratonic rift), and 0.4 Ga (foreland). The 2.1 Ga formed marginal fault has been a very important shield-scale tectonic element and guided both basin evolution and fluid circulation for almost 2 billion years.

LREE mobility in the form of severe LREE loss (up  $> 95\%$ ) has been noticed in many samples from the study area. Monazite, bastnäsite, and to some degree allanite have been the original LREE phases in the LREE depleted samples. During the alteration process, monazite reacted to Th-silicates with variable loss of the LREE to the infiltrating alteration fluid. Most of the remaining LREE was incorporated in Th-poor monazite. In some samples, detrital monazite grains are preserved as inclusions in detrital quartz grains. We propose that alkali-bearing oxidizing fluids started to form in the cratonic sequences, due to diagenetic reactions and a possible contribution

from evaporates, maybe as early as 2.3–2.1 Ga. The alkalinity of the fluids was later intensified by the interaction with alkaline 2.05 Ga source materials before and during the c. 1.91–1.92 foredeep to foreland basin stage.

Basin inversion and metamorphic crystallization occurred between 1.91 Ga and 1.87–1.86 Ga and was probably associated with large amounts of basinal fluids expelled from the deforming basin. Fluid migration at 1.78–1.73 Ga and afterwards was focused along fracture zones. However, the preservation of some broader hydraulic conductivity via microfracture networks and in the metamorphosed coarse-grained sandstone units probably still occurred as late as at 0.4 Ga. The 0.4 Ga event is most prominent of the <1.7 Ga events and is best explained by the occurrence of a shield-wide foreland basin related to the Caledonian orogenic front, which caused heat distribution and fluid circulation extending down to the crystalline basement, especially along faults and fracture zones.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.lithos.2013.05.003>.

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