# Neoarchean sanukitoid series in the Karelian Province, Finland

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ACADEMIC DISSERTATION To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public examination in lecture room D101, Physicum building, on the 5<sup>th</sup> of August 2011, at 12 o'clock noon.

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### Abstract

Sanukitoid series intrusions can be found throughout the Archean Karelian Province of the Fennoscandian shield. All sanukitoids share the same controversial elemental characteristics: they have high content of incompatible elements such as K, Ba, and Sr as well as high content of the compatible elements Mg, Cr, and Ni, and high Mg#. This composition is explained by an enriched mantle wedge origin in a Neoarchean subduction setting. This study concentrates on sanukitoid intrusions and tonalitetrondhjemite-granodiorite series (TTGs) from Finnish part of the Karelian Province. The collected rock samples have been studied in the field and under microscope as well as for their whole-rock (including isotopes) and mineral compositions. The new data together with previously published analyses help us to better understand the petrogenesis, tectonic setting and reworking of the Archean rock units.

TTGs from the Karelian Province form a voluminous series of granitoids and reworked migmatites. This study divides TTG series into two subgroups based on their elemental composition: low-HREE (heavy rare earth element) TTGs and high-HREE TTGs indicating pressure differences in their source. Sanukitoid series is a minor, divergent group of intrusions. These intrusions are variable sized, and the texture varies from even-grained to K-feldspar porphyritic. The elemental composition differentiates sanukitoids from more voluminous TTG groups, the SiO<sub>2</sub> in sanukitoids varies to include series of gabbro, diorite, and granodiorite. U–Pb age determinations from sanukitoid series show temporally limited emplacement between ~ 2745–2715 Ma after the main crust forming period in the area. Hafnium, neodymium, common lead, and oxygene isotopes indicate well homogenized characteristics. Recycled crust has made a variable, yet minor, contribution to sanukitoids, as evidenced by oxygene isotopes and inherited zircon cores.

A proposed tectonic setting for the formation of the sanukitoid series is slab breakoff of oceanic lithosphere in subduction setting, with sanukitoids deriving from an enriched mantle wedge. The proposed setting explains some of the peculiar features of sanukitoids, such as their temporally limited occurrence and controversial elemental composition. Sanukitoids would occur after cessation of the regional growth of Archean crust, and they could be derived from mantle wedge previously enriched by melts and fluids from oceanic crust and sediments. A subsequent event during the Paleoproterozoic Svecofennian orogeny at ~1.9 Ga affected the appearance and microstructures of the rocks as well as caused redistribution of lead between minerals and whole rock. However, the deformation was not able to obliterate the original geochemical characteristics of these sanukitoids

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Publications I-V

### List of original publications

This thesis is based on the following publications:

- I Halla, J., van Hunen, J., Heilimo, E. & Hölttä, P. 2009. Geochemical and numerical constraints on Neoarchean plate tectonics. Precambrian Research 174, 155–162.
- II Heilimo, E., Halla, J. & Hölttä, P. 2010. Discrimination and origin of the sanukitoid series: geochemical constraints from the Neoarchean western Karelian Province (Finland). Lithos 115, 27–39.
- III Heilimo, E., Halla, J. & Huhma, H. 2011. Single-grain zircon U–Pb age constraints of the western and eastern sanukitoid zones in the Finnish part of the Karelian Province. Lithos 121, 87–99.
- IV Heilimo, E., Halla, J., Andersen, T. & Huhma, H. Neoarchean crustal recycling and mantle metasomatism: Hf–Nd–Pb–O isotope evidence from sanukitoids of the Fennoscandian shield. Manuscript submitted to Precambrian Reseach.
- V Halla, J. & Heilimo, E. 2009. Deformation-induced Pb isotope exchange between K-feldspar and whole-rock in Neoarchean granitoids: Implications for assessing Proterozoic imprints. Chemical Geology 265, 303–312.

The publications are henceforth referred to in the text by their roman numerals.

The research project was planned by J. Halla and E. Heilimo.

E. Heilimo's (E.H.) contribution to the papers was as follows:

- I: E.H. did the revision of field work and sampling together with J. Halla. E.H. assumed the main responsibility for writing the sanukitoids' elemental geochemistry section of the manuscript, and the discussion and conclusions were written jointly with J. Halla.
- II: E.H. did the revision field work and sampling together with J. Halla. E.H. assumed main responsibility for interpreting and writing the manuscript, with the help by the co-authors.
- III: E.H. did the field sampling of new samples, hand-picked and photographed the zircons as well as performed the SIMS analyses of all samples. E.H. interpreted the data with H. Huhma and assumed the main responsibility for writing the manuscript with modifications added by the co-authors.
- IV: E.H. was responsible for sampling and sample preparations of new data. The hand-picked zircons from Paper III were used for O analyses, and T. Andersen hand-picked the zircons used in Lu–Hf analyses. The analytical work was done by E.H. with guidance of laboratory staff (T. Andersen supervised Lu–Hf analyses and H. Huhma Sm–Nd and Pb–Pb analyses). E.H. had the main responsibility in interpreting and writing the manuscript with commentary of co-authors, except the Pb–Pb isotopes that were interpreted and written by J. Halla.
- V: EH contributed to the writing of the manuscript together with J. Halla. J. Halla held the main responsibility of the paper.

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### 1. Introduction

#### 1.1. Archean continental crust

The Archean Earth (4.0–2.5 Ga) is considered to have been very different from the modernday Earth. During this period, the Earth changed drastically: most of the continental crust formed and the atmosphere as well as oceans evolved towards the modern, oxidized realms. Transformation from the hotter early Earth with ambiguous tectonics and simple microbial life to a cooler planet with large, rigid continental plates and much more complex life is one of the significant challenges in the Earth Sciences. This study aims to shed light on the Archean plate tectonic processes by studying a minor but geodynamically important group of granitoids and associated rocks, known as the "sanukitoids". The elemental and isotope geochemical as well as dating methods of this study bring information on the source components, metasomatism, geochronology, crustal recycling, and tectonic setting of sanukitoids. These can be used to evaluate the nature of tectonic processes that prevailed in the late Archean (e.g., Rollinson, 2007).

The early evolution of the Earth is stored in the rock record of Archean cratons. Fragments of Archean cratons are dispersed in all present continents around the world. At modern day, the prevailed Archean uppercontinental crust consist mainly grey gneisses and minor greenstones. Whether or not these rock associations are the result of moderntype plate-tectonics has been a long debated question. A valid evidence for Archean plate tectonics, i.e., a well preserved and defined ophiolite complex, is yet to be found, and thus present-day research builds on indirect geochemical evidence. The preservation of samples also yields a challenge, as these successions have often been reworked during post-Archean times.

Archean continental crust is dominated by orthogneisses and minor supracrustal rocks, often referred to as "grey gneisses". The majority of these belong to the tonalitetrondjhemite-granodiorite (TTG) series (e.g., Jahn et al., 1981; Martin, 1994), which is quite rare in post-Archean successions. TTGs are defined as high silica and sodium granitoids, with low contents of ferromagnesian elements:  $SiO_2 > 64$  wt. %, 3 wt. % <  $Na_2O$ < 7 wt. %, and Fe<sub>2</sub>O<sub>2</sub>+MgO+MnO+TiO<sub>2</sub> < 5 wt. % (e.g., Martin et al., 2005). TTGs have been interpreted to be partial melts of basaltic source (Rapp et al., 2003). However, the proposed tectonic settings and the site of partial melting of TTG formation vary from subduction zones (e.g., Martin, 1994; Foley et al., 2002; Martin and Moyen, 2002) to lower parts of thickened crust such as oceanic plateaus (e.g., Smithies 2000; Condie, 2005). Based on experimental works and modelling the pressure of melting varied from <10 kbar to>25 kbar, resulting in significant differences in the residue mineralogy and trace element composition (Moyen and Stevens, 2006). Various subdivisions of the TTG series have been proposed (e.g., Barker, 1979; Luais and Hawkesworth, 1994; Clemens et al., 2006; Champion and Smithies, 2007; Paper I). It is conceivable that, globally, TTGs represent diverse groups that had been formed by different petrogenetic as well as geodynamic processes (Moyen, 2011).

Sanukitoids were identified in the 1980's on compositional grounds as a distinct series of Archean granitoids (Shirey and Hanson, 1984) comprising diorite, quartz diorite, quartz monzodiorite, monzodiorite, granodiorite, and monzogranite as well as more alkaline varieties that lack recent well defined counterparts. The name sanukitoid comes from geochemically similar volcanic rocks of the the Setouchi volcanic belt in Japan, known as sanukites (e.g., Tatsumi and Ishizaka, 1982). Geochemically, the sanukitoid series shows a high mantle signature (high content of Mg, Ni, Cr and high Mg#) and high enriched signature (high LILE; especially K, Ba, Sr) at a given SiO, content (e.g., Lobach-Zhuchenko et al., 2005; Papers I; II). Sanukitoids are found globally on most Archean blocks (Fig. 1), where they form 1-5 % of the continental crust. They were emplaced at ~2.95-2.55 Ga, and typically postdate a long period of episodic and voluminous TTG magmatism (Paper III and references therein).

High contents of compatible elements in sanukitoids indicate mantle origin, whereas enrichment in incompatible elements suggests a significant contribution from a crustal source. The petrogenesis of sanukitoids has been explained by a twostage process in a convergent Archean subduction setting (Stern and Hanson, 1991). The lithospheric mantle wedge was enriched with incompatible elements by melts/fluids from subducted oceanic slab. Afterwards, the enriched mantle wedge was partially melted forming sanukitoid magmas (Stern and Hanson, 1991; Smithies and Champion, 2000; Kovalenko et al., 2005; Martin et al., 2009; Paper II). The mantle source is probably metasomatized and melted as a consequence of a post-



**Figure 1.** Global distribution of exposed Archean crust (Bleeker, 2003) and described sanukitoid intrusions. Sanukitoid magmatism is found in the Karelian Province (e.g., Lobach-Zhuchenko et al., 2005), Greenland (Steenfelt et al., 2005), Superior Province (e.g., Stern et al., 1989; Stern and Hanson, 1991), Amazonian Craton (Oliveira et al., 2009), Limpopo Belt (Laurent et al., 2011), Dharwar Craton (Sarvothaman, 2001), Pilbara Craton (Smithies and Champion, 2000), Yilgarn Craton (Champion and Cassidy, 2007), and Northern China (Wang et al., 2009).

collisional mantle upwelling triggered by slab breakoff or delamination of lower crust (Calvert et al., 2004; Whalen et al., 2004; Lobach-Zhuchenko et al., 2008; Papers I and II).

#### 1.2. Aims of the study

This work describes, compiles, and interprets geological data from Neoarchean sanukitoid series intrusions in the Finnish part of the Karelian Province (Fig. 2). The study seeks answers to the following questions regarding petrogenesis and tectonic setting:

1) Can sanukitoid intrusions be identified as a distinct series, different from TTGs by their elemental composition?

2) What was the emplacement age of sanukitoid intrusions? Are there significant age differences?

3) What do the Hf–Nd–Pb–O isotopes tell about the source components and the contribution of recycled crust in sanukitoid magmatism?

4) What is the possible tectonic setting of sanukitoid magmatism and what triggered partial melting in the source?

5) What were the effects of later Paleoproterozoic reworking on selected sanukitoid intrusions?

#### 1.3. Previous studies

The major rock units of the Finnish part of the Archean Karelian Province and their distribution have long been well established (Wilkman, 1920; Frosterus and Wilkman 1920; Sederholm, 1930; Matisto 1958). Continuous and systematic mapping projects carried out by the Geological Survey of Finland have produced detailed field

knowledge of the area. The first absolute age determinations were done in the early 1960s and they confirmed the Archean age of the Karelian Province (Wetherill et al., 1962; Kouvo and Tilton, 1966). Since then geochronological data have been steadily accumulating and Sm-Nd and Lu-Hf isotope studies have played an important role in recognizing the source components and mantle-crust interaction of the rock units in the area (Patchett et al., 1981; Martin et al., 1983; Huhma, 1986). Several pioneering studies were carried out in Karelian granitoid-migmatite areas by French scholars (e.g., Martin et al., 1983; 1984; Martin, 1987a, 1987b; Querre 1985), while Finnish geologists focused on the economically important greenstone belts (e.g., Luukkonen 1992; Papunen et al., 2009). First sanukitoids from the Karelian Province were described from Russia at the end of the 1990s (Chekulaev, 1999) and three years later from the Finnish side (Halla, 2002). The increasing scientific interest on the Karelian Province can be seen from the amount of studies recently carried out in the area (e.g., Käpyaho, 2006; Käpyaho et al., 2006; 2007; Kontinen et al., 2007; Lauri et al., 2011; Mikkola et al., 2011a; 2011b; Papers, I-V). The advancements in methods and research equipment have led to new extensive sets of geochemical and isotopic data.

# 2. Methods

Accurate geological studies are, first of all, based on field geology. The papers of this work rely on previous mapping and sampling carried out by the Geological Survey of Finland. Previously collected samples were used when available, but also additional mapping and sampling was carried out.



**Figure 2.** Geological map of the Karelian Province and sanukitoid intrusions, compiled from Lobach-Zhuchenko et al. (2005), Paper II, and references therein as well as U–Pb ages of intrusions after Bibikova et al 2005, Paper III and Raate intrusion after Mikkola et al., 2011a. Symbols of the Karelian subprovinces A–Vodlozero, B—Central Karelian, and C—Western Karelian.

Whole-rock elemental analyses (Papers I–III) were performed using X-Ray fluorescence apparatus (XRF) and inductively coupled mass spectrometer (ICP-MS) at the laboratory of the Geological Survey of Finland, Espoo (now Labtium Ltd). Altered samples were avoided in order to gain information from primary geochemical characteristics.

The crushing and pulverizing of the rock samples for isotope analyzes and separation of zircon were performed the Isotope Laboratory for Geology at the Geological Survey of Finland. Direct in situ measurements of isotope ratios in selected mineral samples allow analysis of very small amounts of solid material. For high quality in situ U–Pb (Paper III) and O (Paper IV) analyses of zircon, the high-resolution co-Nordic secondary ion microprobe at the Swedish Museum of Natural History in Stockholm was used. (Nordsim-laboratory; Cameca 1270 and upgraded 1280). In situ Lu–Hf isotopes from zircon were analyzed with the Nu multi-collecton ICP/MS equipped with a New Wave/Merchantek LUV-213 Nd: YAG laser at the Department of Geosciences, University of Oslo (Paper IV). Sm–Nd and Pb–Pb whole-rock (Paper IV) and K-feldspar for Pb–Pb (Paper V) data were acquired using a VG Sector 54 mass spectrometer (the TIMS technique) at the Isotope Laboratory for Geology at the Geological Survey of Finland.

# 3. Review of the original publications

#### 3.1. Paper I

Paper I presents elemental geochemistry of 2.9-2.7 Ga crust-forming granitoids that are thought to be juvenile, i.e., extracted from oceanic crust or mantle, in the Finnish part of the Archean Karelian and Kola Provinces of the Fennoscandian shield. The paper proposes division of sampled rocks based on elemental geochemistry together with physically feasible numerical models and hypothesizes the possible geodynamic/tectonic settings for the origin of the granitoids. The study divides the granitoids into three geochemical groups: (1) low-HREE TTGs with relatively high SiO<sub>2</sub>, low Mg, low HREE, higher Sr, lower Yb<sub>N</sub> and higher Nb/Ta; (2) high-HREE TTGs with slightly lower range of SiO<sub>2</sub>, larger range of MgO contents and higher Cr and Ni contents, lower Sr, higher Yb<sub>N</sub> and lower Nb/ Ta; and (3) a younger group of sanukitoids with medium HREE, high Mg, Ni, and Cr and high K<sub>2</sub>O, Ba, and Sr. The major difference between proposed TTG groups lies in their pressure-sensitive element contents, which indicates high-pressure (>2.0 GPa) garnetbearing basaltic source for the low-HREE group and low-pressure (1.0 GPa) garnet-free

source for the high-HREE TTG. Proposed tectonic scenario for the genesis of the two temporally simultaneous TTG groups is an incipient hot subduction zone underneath a thick oceanic plateau/protocrust. The third group of sanukitoids is proposed to originate by partial melting of enriched (metasomatized) mantle wedge, caused by slab breakoff of oceanic crust in subduction setting. This hypothesis is supported by numerical modeling that implies weaker plates and therefore increased occurrence of slab breakoffs in the Archean.

#### 3.2. Paper II

Paper II compiles and presents new wholerock geochemical data from eight sanukitoid affinity intrusions in the Finnish part of the Karelian Province. The paper proposes diagrams discriminate sanukitoids to from TTGs and describes geochemical characteristics of the Finnish Karelian sanukitoid series. The discussion treats with the tectonomagmatic processes behind the sanukitoid petrogenesis. Studied sanukitoid intrusions are alkali-calcic to calc-alkalic, magnesian, mostly metaluminous, with characteristic sanukitoid features such as elevated abundances of both LILE (K, Ba, and Sr) and compatible elements (Mg, Cr, and Ni) and high Mg#. The general geochemical features of the intrusions were constrained as follows:  $SiO_2 = 55-70$  wt.%,  $Na_{2}O/K_{2}O = 0.5-3$ , MgO = 1.5-9 wt.%, Mg# = 45-65, K<sub>2</sub>O = 1.5-5.0 wt.%, Ba+Sr = 1400ppm, and  $(Gd/Er)_n = 2-6$ . The compositional variation of the sanukitoids could originate from several factors: depth of melting, heterogeneity on the source or polymorphous fractionation. The paper suggests a two-stage petrogenetic process for the petrogenesis of sanukitoids. Firstly, the lithosphere

mantle was enriched by subduction-related fluids/melts. Secondly, the previously enriched mantle was metasomatized again by fluids/melts deriving from upwelling asthenospheric mantle triggered by slab breakoff of a descending slab.

#### 3.3. Paper III

Paper III presents new U-Pb SIMS geochronological data from the Finnish part of the Karelian Province. The paper confirms the occurrence of two temporally separate sanukitoid zones throughout the Province. Inherited zircon cores revealed by the single-grain analyzes allowed also the discussion on crustal recycling and mantlecrust interactions. The sanukitoid series were emplaced between 2745 and 2715 Ma. The study endorses two temporally distinct sanukitoid zones in the Karelian Province (Bibikova et al., 2005) with average ages 2718 Ma for the western sanukitoid zone and 2740 Ma for the eastern zone Abundant number of inherited zircon cores with ages between 3240 and 2750 Ma show longer evolution for the precursors, although the Th/U ratios did not indicate unambiguous source for them. The Karelian sanukitoids were emplaced abruptly after long-lived episodic TTG generation as is the case in other Archean blocks with described sanukitoids

#### 3.4. Paper IV

Paper IV presents Hf, and O isotope data in zircon as well as Nd, and Pb isotope data in whole-rock samples from the Finnish part of the Karelian Province. The data provided by this study is compared with available Nd and Pd isotope data of Karelian sanukitoids. The paper provides information of recycled source components of sanukitoid magmatism. Homogenous initial Hf and Nd data point to well-mixed mantle source(s) with minor contribution of recycled component. Pb-Pb isotope results with their limited scatter shows that crustal contamination was an insignificant process during the emplacement of sanukitoids. Oxygen isotopes from the Karelian sanukitoids show variable  $\delta^{18}$ O values, indicating mainly mantle source, but in some cases the results evidence contributions from high  $\delta^{18}$ O sources (sediments and/or altered upper oceanic crust). This suggests that sanukitoids are formed by mixing of depleted mantle and recycled crustal components. Variable  $\delta^{18}$ O values could be explained by slab breakoff at the end-stage of subduction, because it would allow variable contribution from recycled crust.

#### 3.5. Paper V

Paper V presents a deformation study of sanukitoids based on Pb isotope compositions and microstructures of K-feldspar porhyroclasts in the Nilsiä and Koitere granitoids that are located near the Archean–Proterozoic boundary. In this paper, Pb isotope compositions and microstructures of K-feldspars are used to assess the time and constraints of younger imprint in Archean rocks. The analyzed Pb isotopes suggest low U/Th ratios for the whole rock. The lead isotope ratios correlate with different degrees of mylonitization displayed by the samples and indicate that later deformation-induced Pb isotope redistribution between K-feldspars and Th-rich whole-rock samples occurred at the time of the Proterozoic Svecofennian orogeny at ~1.9 Ga. The microstructures of K-feldspars indicate 400-500 °C temperature conditions during the deformation.

## 4. Discussion

# 4.1. Elemental geochemistry of TTGs and sanukitoids in Finland

#### 4.1.1. TTG series subdivision

The TTG series is a dominant component in Archean (4.0–2.5 Ga) grey gneiss complexes consisting of granitoids, fragments of supracrustal rock types and their melted derivatives (Moyen, 2011). The polyphase metamorphism and migmatitization obscures the interpretation of the origin and tectonic setting of the grey gneisses. The first subdivision of TTGs into two geochemical groups was done by Barker (1979) who divided TTGs into low- and high- Al<sub>2</sub>O<sub>2</sub> groups (separated at 15% Al<sub>2</sub>O<sub>3</sub> and 70% silica) and suggested that the groups were produced by fractionation crystallization or different degree of partial melting. Martin and Moyen (2002) proposed that TTGs were partial melts of subducting oceanic crust and attributed a secular change in their composition to the cooling of the Earth and subsequent transformation from flat to deep subduction allowing interactions with mantle wedge peridotite. However, many early Archean as well as Neoarchean TTGs have observed to lack mantle signatures (elevated Mg, Ni, and Cr), thus showing no evidence of mantle interactions (Smithies, 2000). Regionally, contemporary TTGs may or may not show mantle signature (Almeida, 2010). Furthermore, numerical geodynamic modeling results suggest that flat subduction was not a physically feasible process in the Archean (van Hunen and van den Berg, 2008).

To shed new light on the debated question on the tectonic "site" and setting of the TTGs source, the different elemental groups of TTGs need to be identified. Paper I presents TTG subdivision to low and high HREE TTGs, of which the former group seems to be more voluminous. The division is mostly based on differences in the pressuresensitive HREE contents of TTGs from the Karelian and Kola Provinces. The proposed regional subdivision (Paper I) is partially overlapping with that of the Barberton granite-greenstone terrane (Clemens et al., 2006; Moyen et al., 2007) and of the Pilbara Craton (Champion and Smithies, 2007). Some of studies have separated an enriched or transitional TTG group with high content of K and granodioritic composition (e.g., Champion and Smithies, 2007; Moyen, 2011). Based on a large global dataset and automated groupings Moyen (2011) found four elementally different groups of TTGs. Two of the groups represent high-pressure and low-pressure TTGs being coeval to low and high HREE TTGs suggested by this study (Paper I), respectively, and one being medium pressure, so far not described from the Karelian or Kola Provinces. The enriched/ transitional TTGs have been identified also from the Western Karelian subprovince. The enrichment in K and other LILE could also be related to the Archean metasomatism during migmatization events (Mikkola et al., 2011a). As a whole our knowledge of Archean basement and categorization has increased. A delicate geochemical divisions have been proposed for these Archean granitoids and migmatites (not just grey gneisses or TTGs).

# 4.1.2. Elemental geochemistry of sanukitoid series

The elemental composition of sanukitoid series, which are late tectonic with respect to TTGs, show high content of compatible elements (Mg, Ni, Cr, and high Mg#) and



Figure 3. a)  $(Gd/Er)_p$  vs. MgO and b) Na<sub>2</sub>O/K<sub>2</sub>O vs. Ba+Sr plots illustrating different groups of Archean juvenile granitoids of Karelian and Kola Provinces, illustrating the main differences between TTG groups and sanukitoids and the hypothetic source end-members after Paper I.

also high content of incompatible elements (LILE; especially K, Ba, Sr). The occurrence of sanukitoid series in Archean successions is a global phenomenon, and the geochemical characteristics of the series differ clearly form that of the TTG series.

The first strict geochemical definition for sanukitoids was proposed by Stern et al. (1989) who implied the following criteria:  $SiO_{2} = 55-60$  wt. %, MgO > 6 wt. %, Mg# > 60, Sr > 600–1800 ppm, Ba > 600–1800 ppm, Cr > 100 ppm, Ni > 100 ppm. Later, the term sanukitoid have been used more loosely as a synonym for a series of granitoids and associated rocks having a specific set of characteristics: high Mg Cr, Ni, LILE (K, Ba, Sr) and LREE abundances at variable silica content (e.g., Lobach-Zhuchenko et al., 2005; Papers I, II). Paper II of this work proposes the following elemental limits for discrimination of the sanukitoid series:  $SiO_2 =$ 55-70 wt.%, Na<sub>2</sub>O/K<sub>2</sub>O = 0.5-3, MgO = 1.5-9 wt.%, Mg# = 45-65, K<sub>2</sub>O = 1.5-5.0 wt.%, Ba+Sr > 1400 ppm, and  $(Gd/Er)_n = 2-6$ . This definition emphasizes higher Ba+Sr content and more uniform HREE patterns (Fig. 3) of sanukitoids compared with those of the TTGs.

Some of the compositional variation within the group can be attributed to fractional crystallization processes and to differences in the depth and temperature of melting as well as degree of partial melting (Paper II), but also variation in the source components is viable. Proposed discrimination might be regionally viable, but in a global scale, larger compositional variation within the group may exist, e.g., high Ti-sanukitoids described by Martin et al. (2009).

# 4.2. Geochronology and crustal recycling in sanukitoid series

#### 4.2.1. Geochronology

Compiled ages of sanukitoids from different Archean provinces show that sanukitoids appeared in the rock record at  $\sim 2.95-2.53$ Ga (Fig. 1). In each region, the period of sanukitoid magmatism was very limited and followed soon after the last phase of TTG formation but before crust-derived magmatism (Käpyaho et al., 2006; Mikkola et al., 2011a; Paper III; Fig 4). This indicates that sanukitoids were formed at the end of a collisional stage, before the final stabilization



**Figure 4**. Simplified age distribution diagram of selected well described Archean domains and subdomains, modified after Paper III. Data are collected from the following publications and references therein: Pilbara Craton (Smithies and Champion, 2000), Amazonian Craton (Oliveira et al., 2009), Superior Province (e.g., Davis et al., 2005 and reference therein), Yilgarn Craton (e.g., Champion and Cassidy, 2007), Karelian Province (Bibikova et al., 2005a; Käpyaho et al., 2006; Paper III); Northern China Caton (Wang et al., 2009); Greenland (Steenfelt et al., 2005).

of the crust. Therefore sanukitoids might evindence the accretion of Neoarchean supercontinent Kenorlandia (e.g., Bleeker, 2003). The temporal and spatial differences of sanukitoid intrusions within the Karelian Province (Lobach-Zhuchenko et al., 2005; Bibikova et al., 2005; Paper III; Fig. 2) raises a question of whether the temporal difference is caused by two or more separate processes or by a continuum of a differing process during the accretion. The inherited zircons in the Karelian sanukitoids indicate a contribution from a recycled component in the genesis of sanukitoids (Bibikova et al., 2005; Paper III).

#### 4.2.2. Crustal recycling

Plenty of radiogenic Hf, Nd, and Pb isotope works on Neoarchean sanukitoid series and other Archean lithologic units have been carried out in the Karelian Province in the Fennoscandian Shield and the Superior as well as the Slave Provinces in the Canadian Shield (e.g., Corfu and Stott, 1993; Corfu and Stott, 1996; Davis et al., 2005; Kovalenko et al., 2005; Halla, 2005; Käpyaho et al., 2006; Lauri et al., 2011; Paper IV). These studies have shown that the Nd and Hf isotope data point to a mantle source with variable contribution from continental crust. Comparison of the radiogenic isotope



**Figure 5.** Schematic model of sanukitoid formation in subduction zone showing subduction related slab breakoff as plausible mechanism to produce the variable  $\delta^{18}$ O values with mixing of mantle and variable amount of high  $\delta^{18}$ O sources (upper oceanic crust and and sediments). Picture modified from King et al. (1998) include slab breakoff (Paper IV and reference therein).

compositions from the mantle-derived Karelian sanukitoids with those from the lithologic units of the Superior and Slave Provinces indicate well-mixed sources and reflect recycling of sediments from crustal reservoirs of different age during subduction processes. The homogeneous initial Pb isotope compositions exclude the possibility of large-scale upper-crust contamination during emplacement in Karelia (Paper IV).

# 4.3. Implications to tectonic setting and the source components of sanukitoid series

There is a general consensus that sanukitoids are originated from subcontinental lithospheric mantle (SCLM) enriched by subduction related fluids and/or melts (Stern et al., 1991). Subduction-related enrichment and mixing in the mantle wedge explains the elemental characteristics (enrichment in both compatible and incompatible elements) for sanukitoids series. The interaction between subduction fluids and the peridotitic mantle can produce phologopite containing LILE (Wyllie and Sekine, 1982). However, detailed components of the mixing process as well as the trigger mechanism of the partial melting are debated. Recently experimental and modeling studies endorsed the subduction zone origin for sanukitoids. Oliveira et al. (2010) showed that sanukitoids have elevated redox state and high volatile contents, which are similar to modern day subduction zone

related magmas. Rapp et al. (2010) showed that reaction between TTG melt and olivine bearing peridotite can produce a sanukitoid composition, albeit geochemical modeling by Laurent et al. (2011) suggested that subducted sediments might have contributed in the genesis.

A breakoff an oceanic subducting slab has been suggested as the trigger of the sanukitoid magmatism (Calvert et al., 2004; Whalen et al., 2004: Lobach-Zhuchenko et al., 2008; Papers I, II; Fig 5). Sometimes also lower crustal delamination has been discussed as an alternative mechanism (Whalen et al., 2004; Paper II). Combination of geochemical data and numerical models in Paper I support a slab breakoff origin for the formation of sanukitoids. The oceanic crust has been proposed to be the component that contributed to the enrichment of the sanukitoid source: some of the researchers also discuss the possibility of sediment contribution in the source of sanukitoids (King et al., 1998; Halla, 2005). Isotope data from sanukitoid series in the westernmost part of the Karelian Province in eastern Finland suggest a variable contribution from a high  $\delta^{18}$ O source (altered upper part of oceanic crust or/and sediments) in sanukitoid series (Paper IV), some authors even discuss about the possibility of carbonatite material contribution (Steenfelt et al., 2005; Lobach-Zhuchenko et al., 2005; Papers I, IV). Karelian data suggest that sanukitoids represent comagmatic series in which amounts of recycled material from subducting slab and sediments vary between intrusions. A slab breakoff at the end stage of subduction could explain the temporal occurrence of sanukitoids after the main crust-forming period and recycling of crustal material into the mantle source of sanukitoids.

# 4.4. Paleoproterozoic reworking of the Karelian Province

One of the problematic issues of Archean crustal evolution is later reworking of the crust, especially in the vicinity of the boundary with younger areas. The westernmost part of the Karelian Province in Finland has been variably affected by thermal overprinting and deformation during Paleoproterozoic time by Svecofennian orogeny from the southwest (e.g., Nironen et al., 1997). This generally convergent orogeny formed large areas of Paleoproterozoic crust next to the Archean nucleus. The effects of reworking are often observed in the field, but there are only few targetted studies on the issue. An extensive study of the tectonothermal overprinting throughout the Finnish part of the Karelian Province, based on K-Ar age determinations of biotites and hornblendes (Kontinen et al., 1992), showed that most of the Archean basement areas, excluding granulite facies blocks, were heated up to 300 °C and large areas over 500 °C at 1850-1800 Ma due burial beneath over-thrust nappes. A study by Pajunen and Poutianen (1999) described metasomatic-metamorphic overprint zones of Archean tonalitic kyanite bearing gneisses based on petrographical, structural evidences, mineral chemistry, fluid inclusions, and U-Pb xenotime datings. The study reported peak conditions at 600-620 °C and 4-5 kbar. The Paleoproterozoic deformation is supported by observed episodic Pb loss of K-feldspars (Paper V). The deformation microstructures of K-feldspars indicate ~400-500 °C conditions in the Koitere and Nilsiä area. Similar major and trace element contents of both deformed and undeformed samples of the Koitere complex (Halla, 2002; Paper V) have been observed, despite of the Paleoproterozoic deformation, indicating that sanukitoid intrusions have retained close to their original elemental characteristics.

## 5. Conclusions

This study provides new elemental and isotope geochemical as well as geochronological data on the sanukitoid series in the Finnish part of the Karelian Province. The results lead to the following conlusions:

1. Sanukitoid series intrusions, with different size and variable textures from even-grained to porphyritic, can be found throughout the Karelian Province consisting of subprovinces of different age.

2. Sanukitoid intrusions can be identified from TTG series (both low and high-HREE groups) based on their elemental composition: high content of LILE (K, Ba, Sr) and high content of mantle-compatible elements (Mg, Cr, Ni) and high Mg#.

3. The sanukitoid intrusions were emplaced after the main phase of crust forming process. The Karelian sanukitoids were emplaced between 2710–2745 Ma as two zones western and eastern, showing age and geographical differences.

4. The observed inherited zircon cores in sanukitoids reveal new details on the evolution of the precursor of the series.

5. The homogenous (on intrusion scale) initial radiogenic isotope ratios indicate effective mixing processes in the source of sanukitoid series.

6. Variable oxygene isotope ratios in zircons from sanukitoid series indicate a mantle source with minor and variable contribution from high  $\delta^{18}$ O source such as sediments and altered upper oceanic crust.

7. A viable tectonic setting for sanukitoids is a breakoff of an oceanic slab at the end stage of subduction. This would explain the temporal occurrence of sanukitoids after the main peak of crust formation as well as evidence for on enriched mantle source that is regarded as the source of sanukitoid.

8. Redistribution of Pb isotopes and deformation microstructures of K-feldspars correlate in the Koitere and Nilsiä areas, indicating Paleoproterozoic deformation at low to moderate temperatures (400–500 °C) and variable strain conditions.

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