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by Juha A. Karhu

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PALEOPROTEROZOIC EVOLUTION OF THE CARBON ISOTOPE RATIOS OF SEDIMENTARY CARBONATES IN THE FENNOSCANDIAN SHIELD

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JUHA A. KARHU

with 43 figures, 12 tables and 2 appendices

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$\delta^{13}C$ and $\delta^{18}O$ values of calcite and dolomite have been determined for 229 sedimentary carbonate rock samples from Paleoproterozoic supracrustal belts of the Fennoscandian Shield. In addition, $\delta^{13}C$ values of organic carbon have been analysed for 28 black shale samples collected from formations directly connected to selected sedimentary carbonate units.

The distribution of $\delta^{13}C$ values of total carbonate is clearly bimodal, showing a pronounced maximum at about 1‰ and another less distinct maximum at about 10‰. The $^{13}C/^{12}C$ ratios of sedimentary carbonates vary systematically within individual stratigraphic sequences, and exhibit broadly similar evolutionary patterns in widely separated supracrustal belts. Relying on formations for which the time of deposition could be estimated from radiometric age data, a carbon isotope evolution curve was constructed for the time period from 2.5 to 1.9 Ga. The most conspicuous and stratigraphically useful feature of the curve is the interval from about 2.2 to 2.1 Ga, which is represented by highly ^{13}C-enriched sedimentary carbonates with $\delta^{13}C$ values in the range 10±3‰. These are followed between 2.11 and 2.06 Ga by a sharp, almost 10‰ drop in the $\delta^{13}C$ values of carbonates, while from that time until 1.9 Ga the $\delta^{13}C$ values remain in the range 0±3‰.

Carbon isotope compositions for organic carbon in black shales associated with the ^{13}C-enriched carbonates show large variation. Most of the $\delta^{13}C$ values fall in the range -19±3‰, suggesting a comparative ^{13}C-enrichment in the coexisting organic matter, but some samples show more negative $\delta^{13}C$ values, down to as low as -43‰. In contrast to the majority of the samples, these strongly ^{13}C-depleted black shales have not been observed in direct contact with the carbonate units, and they seem to result from local predominance of processes producing extremely light organic carbon, possibly through methylotrophic pathways.

It is suggested that the positive carbon isotope shift observed in sedimentary carbonates of the Fennoscandian Shield was related to an increased relative rate of burial of organic matter on a global basis. The shift was possibly enhanced by local burial of isotopically unusually light organic matter. As high burial rates of organic carbon are probably followed by a large flux of free oxygen, the positive carbon isotope shift may be fundamentally connected with the significant rise in atmospheric oxygen levels at about 2.0 Ga.

Key words (Georef Thesaurus, AGI): carbonate rocks, black schists, carbon, isotope ratios, C-13, stratigraphy, carbon cycle, paleoatmosphere, oxygen, Baltic Shield, Proterozoic, Paleoproterozoic, Finland, Sweden, Russian Federation

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INTRODUCTION

For as long as life has existed on Earth, carbon has been buried in sediments both as inorganic carbon, precipitated in the form of carbonates, and as biogenic carbon, which is deposited in sediments in the form of organic matter. The fraction buried as organic carbon has originally been produced during biological carbon fixation processes, which are accompanied by significant fractionation of carbon isotopes (Rankama, 1948; Craig, 1953; Park & Epstein, 1960).

If the relative proportions of burial of organic and inorganic carbon change, then this is also reflected in the isotopic compositions of inorganic and organic carbon (Broecker, 1970). It is somewhat surprising, therefore, that throughout geologic history the isotopic composition of carbon in carbonates and in organic matter have remained fairly close to the compositions found in modern sediments (Schidlowski et al., 1983). This stability implies that biogenic carbon fixation has been operating since earliest Archean times and that the relative proportions of inorganic and organic carbon incorporated into sediments have remained nearly constant (Schidlowski et al., 1983).

The period around 2.0 Ga appears to be one of the big milestones in the evolutional history of the biosphere. According to geochemical indicators, for instance, it is characterized by a dramatic increase in the O_2 content of the atmosphere (Holland et al., 1989; Walker et al., 1983; Cloud, 1980). The oldest microfossils interpreted as eukaryotes also date from this time interval (Han & Runnegar, 1992). Because of the intimate relationships between oxygen production and the biological and geochemical cycles of carbon, it may indeed be anticipated that these remarkable changes may have left some kind of signature within the isotope systematics of carbon.

Most of the carbon isotope compositional data reported from Paleoproterozoic sedimentary carbonates fall within the general range of modern marine carbonates (Veizer et al., 1992a, 1992b). However, Paleoproterozoic limestone and dolomite formations characterized by ^{13}C-enriched carbon isotope compositions also exist and have been recorded from Zimbabwe (Schidlowski et al., 1976), Gabon (Gauthier-Lafaye & Weber, 1989), Scotland (Baker & Fallick, 1989a), Australia (McNaughton & Wilson, 1983) and also from various parts of the Fennoscandian Shield (Baker & Fallick, 1989b; Karhu, 1989; Yudovich et al., 1991; Galimov et al., 1975).

The depositional ages of these successions are not very well constrained, and at the moment it is impossible to ascertain, whether or not these ^{13}C-enrichments represent a single global event or local and diachronous perturbations. The former possibility was suggested by Baker and Fallick (1989b) and the latter by Schidlowski et al. (1976) and Yudovich et al. (1991).

The Archean cratonic nucleus in the central and eastern Fennoscandian Shield preserves a relatively continuous sequence of rifting episodes and sedimentation that commenced at about 2.5 Ga. Therefore, the Fennoscandian Shield provides good opportunities for studying and assessing the nature and significance of Paleoproterozoic changes. Unfortunately, however, sedimentary carbonates are, due to unfa-

vourable environments, very rare in the sequences older than 2.2 Ga. From 2.2 Ga to 2.1 Ga carbonate occurrences became more abundant and finally at about 2.1 Ga large areas of the Archean craton were covered by extensive carbonate formations.

This work presents and discusses carbon and oxygen isotope analyses from sedimentary carbonates from various Paleoproterozoic sedimentary units of the Fennoscandian Shield, including several well-studied stratigraphic successions. Many of them contain ^{13}C-enriched carbonates and collation of the results shows consistent evolutionary trends in $^{13}C/^{12}C$ ratios for different supracrustal belts. Therefore, carbon isotope studies offer a potential method of correlating Paleoproterozoic sedimentary formations within the Fennoscandian Shield. Preliminary results from this study have been published by Karhu (1989, 1992) and isotope data for the Kola Peninsula area in Russia have been given by Karhu and Melezhik (1992).

GEOLOGIC OVERVIEW AND STRATIGRAPHIC NOMENCLATURE

Major tectonostratigraphic units

The continental crust of the Fennoscandian Shield can be divided into two major structural units (Fig.1), namely the Archean Domain in the northeastern part of the shield and the Svecofennian Domain in the southern and central part of the shield (Gaál & Gorbatschev, 1987). The former consists predominantly of rocks formed between 2.9 and 2.6 Ga ago, while the latter represents a Paleoproterozoic crustal growth event at about 2.0–1.75 Ga, in which new mantle material was accreted to the existing continental crust (Patchett et al., 1981; Patchett & Kouvo, 1986; Huhma, 1986) in an event known as the Svecokarelidic (Simonen, 1980) or Svecofennian (Gaál & Gorbatschev, 1987) orogeny.

The Archean Domain may be further divided into the Karelian, Belomorian and Kola Peninsula Provinces (Gaál & Gorbatschev, 1987). The whole Archean Domain is underlain by late Archean granitoids and greenstone belts, but the Karelian and Kola Peninsula Provinces contain numerous remnants of Paleoproterozoic platform cover sequences and intracratonic thrust and fold belts (Fig. 1). The most remarkable Paleoproterozoic thrust and fold belts include the Lapland Granulite Belt and the Pechenga–Varzuga Belt, which have been interpreted to as representing Paleoproterozoic accretionary belts associated with the convergence of disparate late Archean continental blocks (Barbey et al., 1984; Berthelsen & Marker, 1986a). The Paleoproterozoic supracrustal successions deposited on the Archean Karelian Province (Fig. 1) are collectively known as the Karelian formations (Eskola, 1925; Meriläinen, 1980).

The Svecofennian Domain includes volcanic sequences interpreted as island arc or volcanic continental margin settings and large graywacke dominated sedimentary deposits (e.g., Simonen, 1953). The original geologic features of the Svecofennian Domain have been largely obscured by granitoid intrusions and tectonic activity.

Traditional stratigraphic nomenclature

The Karelian formations deposited on the Archean basement have been traditionally divided into three consecutive successions, which have been called the Sariolian, the Jatulian and the Kalevian groups (Eskola, 1925; Väyrynen, 1933; Meriläinen, 1980; Simonen,

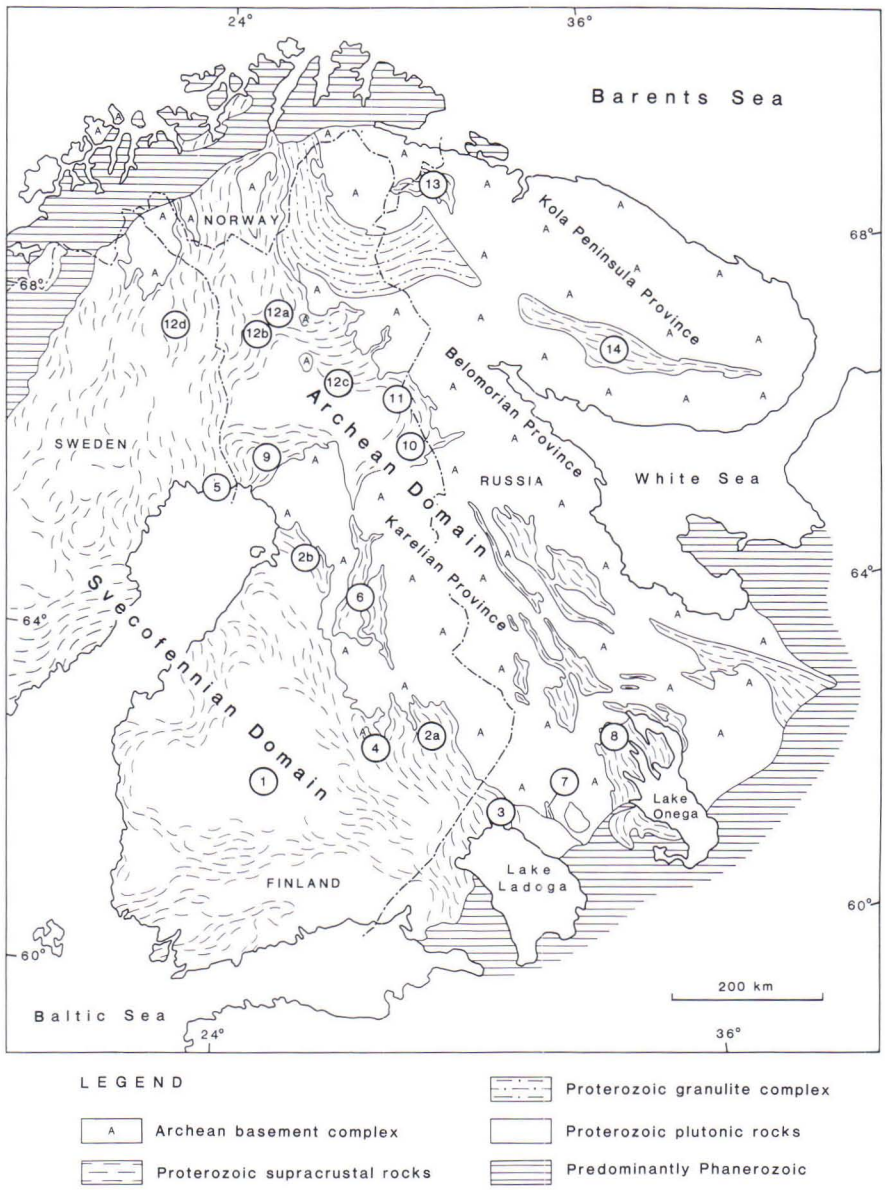

Fig. 1. Geological map of the central and northeastern part of Fennoscandian Shield, mainly after Gorbunov & Papunen (1985). Numbers indicate study areas: 1. Svecofennian Domain, 2a. North Karelia Schist Belt, 2b. Northern Ostrobothnia Schist Belt, 3. Pitkäranta area, 4. Kuopio area, 5. Kalix Greenstone Belt, 6. Kainuu Schist Belt, 7. Tulomozero area, 8. Lake Onega area, 9. Peräpohja Schist Belt, 10. Kuusamo Schist Belt, 11. Salla Schist Belt, 12a. Karasjok–Kittilä Greenstone Belt, 12b. Kittilä–Kolari area, 12c. Pyhätunturi area, Pelkosenniemi, 12d. Western Lapland area, 13. Pechenga Belt, 14. Imandra–Varzuga Belt.

1980; Laajoki, 1986). However, in recent years the value of these broad terms has been questioned. Firstly, there has been no consensus about the definition of these units, and they

have been used to refer to both time-stratigraphic units and lithofacies associations (Laajoki, 1986). Secondly, recent studies have designated more local and formal lithostratigraphic units at the formation and group level, which has largely rendered the traditional broad classification obsolete for the purpose of correlation throughout the shield (Laajoki, 1988).

In spite of the reservations expressed above, the traditional terms, Sariolian, Jatulian and Kalevian, are still used here, as they clearly remain useful in large scale studies. Nevertheless, they are not used as formal lithostratigraphic units, but as informal parastratigraphic units in the sense of Krumbein and Sloss (1963, p. 333). This kind of usage has been encouraged by Schoch (1989, p. 163), who observes that many extremely useful stratigraphic units are never formalized or cannot be formalized, because they do not fit into the conventions used for instance in the International Stratigraphic Guide (Hedberg, 1976).

Parastratigraphic units of the Karelian formations

According to Krumbein and Sloss (1963), there are two types of criteria that are applied to define parastratigraphic units. One is based on special attributes, like for instance trace element composition, and the other on marker horizons. In fact, the traditional stratigraphic units in current use are very close to marker-defined parastratigraphic units, except that some boundaries are not well defined.

Here the stratigraphic classification of the Karelian formations will be adopted largely from Sokolov (1980), who based his classification on earlier works of Ramsay (1902, 1906), Metzger (1924) and others. In essence this is a marker-defined parastratigraphic classification, which in addition to the traditional groups of the Karelian formations includes a new Ludian group, largely based on the well preserved and only weakly deformed succession in Russian Karelia. The key horizons marking group boundaries will be reviewed in the following.

The Sariolian group, including the Sumian formations in Russian Karelia (e.g. Gaskelberg et al., 1986), contains the lowermost supracrustal units, which have been deposited unconformably on the Archean basement. Deposition of these was followed by an intensive weathering period, and as a result a widespread weathering crust was formed. This paleosol is understood as separating the Sariolian group from the overlying Jatulian group (Sokolov, 1980; Meriläinen, 1980). Since the weathering crust has been found from all localities, where Jatulian formations are common (Negrutsa et al., 1986; Marmo, 1992), the lower boundary of the Jatulian group seems to be well defined, irrespective of whether it is synchronous or diachronous.

The boundary separating the Jatulian group below from the Ludian formations above corresponds to the Mesojatulian–Neojatulian boundary of Metzger (1924) and the Jatulian–Onegian boundary of Ramsay (1902, 1906). It coincides with an abrupt facies change from pink and light colored quartzites and dolomites to grey and green colored graphitic shales and impure dolomites. With respect to burial of carbon the Jatulian–Ludian boundary marks a change from conditions where carbon is deposited in the form of carbonates to a system in which carbon is removed from the basin mainly in the form of organic matter. This Jatulian–Ludian distinction is important when the unusual carbon isotope systematics of the Karelian sediments are discussed.

The Ludian formations are typically found in the synclinorial cores of Jatulian outliers in the areas around Lake Onega, Tulomozero, Suojärvi and Kuusamo (Galdobina & Melezhik, 1986). The sharp facies change marking the Jatulian–Ludian boundary is also evident in the stratigraphic section of the Kiihtelysvaara area in Finland reported by Pekkarinen (1979).

It should be noted that the Ludian group is not equivalent to the Marine Jatulian facies of Väyrynen (1933), because in addition to the Neojatulian unit, the Marine Jatulian was defined to include the largely dolomitic Mesojatulian unit of Metzger (1924) as well.

The upper boundary of the Ludian is marked by a change to massive Kalevian graywackes.

MATERIALS AND METHODS

Sample selection

Sedimentary carbonates were collected for isotopic analysis from different Paleoproterozoic supracrustal formations in the central and eastern Fennoscandian Shield. Because pure carbonate rocks are known to retain their carbon isotope compositions better than those containing a larger proportion of silicates, all samples were inspected visually and only those sedimentary carbonates which were estimated to contain more than about 80% carbonate were chosen for analyses.

Samples analysed in this work were obtained from different sources. Some represent field samples from various current Geological Survey of Finland mapping programs, others are representative specimens from limestone and dolomite quarries donated by mining companies. The Geological Museum of the University of Helsinki has a good collection of Paleoproterozoic metasediments from eastern Karelia collected at the beginning of this century and a few samples from various subareas were selected for this work. In addition, samples were collected specifically for this study from outcrops and from the National drill core archives of the Geological Survey of Finland. Brief descriptions, sample localities and original sample codes are given in Appendix 1.

A few samples were rejected after isotopic analysis, if they either contained less than 75% carbonate or the measured $\delta^{18}O$ value of oxygen in carbonate was below 13‰ (SMOW). Both provisions were essential in avoiding samples affected considerably by decarbonation reactions. The latter prerequisite was, in addition, necessary in order to eliminate extensively exchanged and hydrothermal carbonates. If oxygen isotopes are shifted down from their original Paleoproterozoic $\delta^{18}O$ values of about 22 to 24‰ (SMOW) (Veizer, 1992a, b), indicating extensive exchange, carbon isotopes may also have been shifted, as carbon and oxygen isotope ratios in carbonates often show mutually correlated depletions in ^{13}C and ^{18}O (Valley, 1986).

The data set also includes a few samples from important key formations, which do not fulfil the above mentioned requirements. Their preservation, including arguments suggesting a sedimentary origin, will be discussed separately.

Determination of dolomite-calcite ratios

Isotope analytical methods are chosen according to the carbonate species in question. Therefore, an aliquot of the sample powder was used to routinely determine the proportion of dolomite in the total carbonate by a semi-quantitative X-ray diffraction method.

These XRD methods are usually based on counting the intensities or the peak areas of the main reflections of calcite and dolomite (Royse et al., 1971), and the numbers are then converted into dolomite weight percentages using calibration curves. The published calibration equations of Tennant & Berger (1957), Weber & Smith (1961) and Royse et al. (1971)

all show small differences from each other, with none of them giving satisfactory results close to the end member compositions. For instance, applying the curve of Royse et al. (1971) to pure dolomite samples gave dolomite contents that were systematically too high, ranging from 102 to 103%.

Because pure or nearly pure dolomite is typical of Precambrian sedimentary formations, it was decided to investigate the possibility of improving existing calibrations. For these purposes synthetic mixtures of pure calcite and dolomite were prepared from pure natural dolomite (sample C-119D of this study) mixed with either commercial calcite reagent (Merck) or natural calcite (C-117). Natural carbonates used for the calibration were essentially free from silicate impurities and the acid residues were <0.1% in both cases.

In the following, first the theoretical form of the calibration curve is derived, and then the synthetic mixtures of calcite and dolomite are used to estimate the unknown parameter in the equation.

The diffraction line intensities of a phase (I_i) are related to the weight fraction (X) and density (ρ) of the phase and to the mass absorption coefficient of the mixture μ_m:

$$I_i = K_i X_i / \rho_i \mu_m \qquad \text{(Eq. 1)},$$

where K_i is a constant for the given phase and the chosen diffraction line (Snyder & Bish, 1989). In a mixture of two phases the mass absorption coefficient is eliminated by calculating the ratio of the diffraction line intensities for phases i and j:

$$I_i / I_j = K X_i / X_j \qquad \text{(Eq. 2)},$$

where the constant K includes the K_i/K_j term and the ratio of the densities. Up to this point the derivation is equal to the calculation of diffraction line intensity ratios in the internal-standard method (Snyder & Bish, 1989).

However, in a mixture of two phases, the weight fractions are expressed as percentages that add up to 100%. Substituting this into

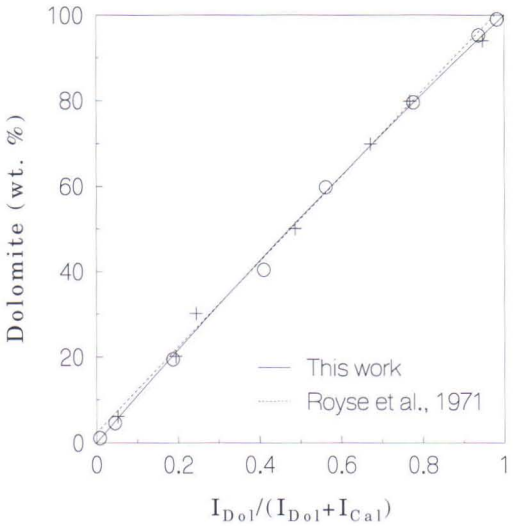

Fig. 2. Calibration curve for the determination of the weight percentage of dolomite in a mixture of calcite and dolomite, using XRD peak-height intensities compared to the linear calibration line of Royse et al. (1971). Also shown are the results from the synthetic calcite dolomite mixtures prepared from natural dolomite and natural calcite (crosses) and from natural dolomite and commercial calcite reagent (circles).

Equation 2, rearranging and solving X_i leads to

$$X_i = 100Y_i / (Y_i + K(1-Y_i)) \qquad \text{(Eq. 3)},$$

where $Y_i = I_i/(I_i+I_j)$. This equation represents the locus of a rotated hyperbola passing through (0,0) and (100,1) and describes the general relation of XRD intensities to weight percentages in two phase mixtures.

The unknown coefficient (K) for dolomite-calcite mixtures (dolomite = i, calcite = j) was estimated by fitting the equation derived above to intensity data from synthetic calcite dolomite mixtures. The diffraction line intensities of the main reflections were measured using Cu-K_α radiation, first scanning the 2θ region from 27° to 32° and then counting the peak intensities at 2θ angles of about 29.4° and 30.8° for calcite and dolomite, respectively.

A nonlinear iterative program gave a best fit to the theoretical curve with K = 0.9017, and the resulting graph is shown in Figure 2. Also shown are the dolomite proportions and the intensity ratios of the synthetic mixtures.

Crosses indicate mixtures in which the natural calcite was used, and circles refer to admixtures of reagent grade calcite and natural dolomite. In the central area the calibrated curve agrees remarkably well with the linear calibration of Royse et al. (1971) and differences are evident only in the proximity of the end member compositions.

At best this method is a rapid way of determining the proportion of dolomite in a calcite-dolomite mixture in the total range of 0–100%. Based on repeated experiments, accuracy is about ±5% when calcite and dolomite are present in similar amounts, but is better than 1% as end member compositions are approached. Nevertheless, the results are only semi-quantitative. Firstly, as Runnels (1970) has pointed out, chemical variations in carbonates can lead to large shifts in the intensities of the main reflections, which will lead to errors in the apparent proportions. Secondly, other variables, such as grain size and preferred orientation may affect the intensity of the diffracted beam. Thirdly, if silicate impurities are present, interfering diffraction lines may cause errors.

Isotopic notation and expressions

Carbon and oxygen isotope compositions are measured as isotope ratios, $^{13}C/^{12}C$ and $^{18}O/^{16}O$ respectively, which are reported relative to an international standard using so-called delta notation. For carbon the $^{13}C/^{12}C$ ratio is given as a per mil deviation from the PDB standard (Cretaceous belemnite of the Peedee formation, South Carolina, USA):

$$\delta^{13}C = 1000(R_{SA}/R_{PDB} - 1),$$

where $R_{SA} = {}^{13}C/{}^{12}C$ for the sample and $R_{PDB} = {}^{13}C/{}^{12}C$ for the PDB standard. The $\delta^{18}O$ value is defined similarly:

$$\delta^{18}O = 1000(R_{SA}/R_{ST} - 1),$$

where $R_{SA} = {}^{18}O/{}^{16}O$ for the sample and $R_{ST} = {}^{18}O/{}^{16}O$ for the standard, which may be either the PDB or the SMOW standard (standard mean ocean water). In this work the oxygen isotopic results are given relative to the SMOW scale, but they are easily converted to the PDB scale using a simple, linear equation (Friedman & O'Neil, 1977).

When the isotopic composition of carbon in two samples is compared, the one with a higher $\delta^{13}C$ value is enriched in ^{13}C relative to the other sample. However, the carbon isotopic composition of sedimentary carbonates has generally remained approximately in the range 0±3‰ throughout geologic time (Schidlowski et al., 1983), and this value may also be used as a reference for sedimentary limestones and dolostones. In this work sedimentary carbonates showing these isotopic signatures will be referred to as normal sedimentary carbonates. The more unusual carbonates with $\delta^{13}C > 3‰$ are referred to as being enriched in ^{13}C with the assumption that the reference is made to normal sedimentary carbonates.

Isotopic analysis of calcite

The carbon and oxygen isotopes in pure calcite samples, with < 2% dolomite in the carbonate fraction, were measured using the conventional phosphoric acid method at 25°C (McCrea, 1950). To assure essentially complete yields, sample powders were sieved to <70 µm grainsize, and then about 20 mg of powder was weighed into the reaction vessels, and about 2 cl of >100% phosphoric acid (Wachter & Hayes, 1985) was added to the side arm of the vessel. The vessels were evacuated for >10 hours under high vacuum at 25°C, after which

the acid was poured on to the sample, and the vessel was placed back in the thermostated water bath for >16 hours. The following day the liberated CO_2 was collected in a liquid nitrogen cold trap and then transferred to a manometer using ethanol at about -80°C to remove water vapour. Finally the CO_2 sample was collected in a sample tube, ready for analysis in a mass spectrometer.

During the phosphoric acid reaction all carbon in calcite is liberated as CO_2, but only two thirds of the oxygen is bound within CO_2. Therefore, analysis of the carbon isotope ratio of CO_2 gives directly the isotopic composition of the source calcite. However, oxygen isotopes will be fractionated between the original calcite and the CO_2 produced by reaction with phosphoric acid, and this fractionation factor must be known at the temperature of reaction. For calcite reacted at 25°C the generally accepted fractionation factor of 1.01025 (Friedman & O'Neil, 1977) was used.

Calibration to the PDB and SMOW scales was made through NBS-20 (Solenhofen limestone), assuming the isotope ratios given for it by Craig (1957). The precision of the $\delta^{13}C$ and $\delta^{18}O$ determinations from calcite is better than 0.05‰. In the course of this study, between 1988 and 1992, 13 analyses of the NBS-19 standard gave a mean $\delta^{13}C$ value of 1.95±0.02‰ (1SD) and a $\delta^{18}O$ value of -2.27±0.04‰ (1SD, PDB). These agree well with the values of 1.93‰ and -2.19‰, respectively, reported by Coplen et al. (1983).

Isotopic analysis of dolomite

Dolomite reacts very slowly with phosphoric acid at 25°C, and even after a reaction time of one week the yields are typically incomplete. Such reaction times are very impractical, and there may, in addition, be small systematic differences in the isotopic composition of the evolved CO_2 gas in the course of the reaction (Walters et al., 1972). Therefore, an extraction method that gives essentially complete yields in shorter time is preferable, and this in fact is possible at higher reaction temperatures (Rosenbaum & Sheppard, 1986).

In this work dolomite samples, with > 98% dolomite in the carbonate fraction, were reacted with phosphoric acid at 100°C, a value chosen because this temperature is readily achieved with a high degree of accuracy in a boiling water bath and the transfer of heat from the water bath to the vessel is rapid. In addition, essentially complete yields are obtained in one hour, and the precision of the results seems to be better than in the 25°C experiments.

For analysis dolomite samples were sieved to < 40 µm grainsize and degassed in a vacuum line at room temperature for > 6 hours. The acid was poured on to the carbonate, and the vessel was immediately placed in a boiling water bath. Unlike calcites, the dolomite samples were not pre-equilibrated at the reaction temperature. This is also the method recommended by Rosenbaum & Sheppard (1986), who observed no variation in the isotopic results with respect to the pre-equilibration temperature. Following reaction, the vessels were transferred back to the vacuum line and the evolved CO_2 was collected in the normal way.

The oxygen isotope fractionation factor between dolomite and acid extracted CO_2 at 100°C was given by Rosenbaum & Sheppard (1986) as 1.00913. Since there are small differences between the extraction procedures used by them and those used in this work, the dolomite laboratory standard (C-119-D, Tytyri) was, in addition, analysed using the conventional phosphoric acid method at 25°C with a reaction time of about one week, and the isotopic results were then compared with each other.

Five replicate measurements at 25°C with a reaction time of one week gave a mean $\delta^{13}C$

value of 0.76±0.02‰ (1SD) and a $\delta^{18}O$ value of 23.76±0.33‰. For nine analyses at 100°C the mean $\delta^{13}C$ value was 0.74±0.03‰ and the $\delta^{18}O$ value was 23.36±0.06‰. Here a phosphoric acid fractionation factor of 1.01110 (Clayton et al., 1968) was used to calculate the isotopic results of dolomite oxygen at 25°C. The carbon isotope results are equal within error limits and the reproducibility of the results is better than 0.05‰ in both cases. The $\delta^{18}O$ compositions measured using the 25°C reaction appear to be on average about 0.4‰ heavier than the results from the 100°C experiments, although the accuracy of the former results is relatively poor. The difference in the $\delta^{18}O$ values could be caused by uncertaintity in the phosphoric acid fractionation factors.

Analysis of mixed calcite-dolomite samples

Analyses of coexisting calcite and dolomite may be made without physical separation of the phases (Epstein et al., 1964). The method is based on the different reaction rates of calcite and dolomite with phosphoric acid, which enables sequential collection of CO_2 first from calcite and then from dolomite. However, several precautions must be taken to get an effective separation of the phases and to minimize cross mixing. The reaction times should be optimized, and since particle size affects reaction rates, the particle size range should also be limited (Walters et al., 1972).

For mixed samples containing both calcite and dolomite, a modification of the method of Epstein et al. (1964) was used. The sample powder was first sieved to < 40 µm grainsize. Then the finest size fractions were removed by washing the powder several times with distilled water, relying on the different relative settling velocities of the particles. After the treatment the grain size of the samples was limited to a range from about 20 to 40 µm.

From 20 to 40 mg of sample was degassed with > 100% phosphoric acid at 25°C for at least 5 hours. Then acid was poured on to the carbonate and CO_2 evolved during the next 1.5 hours was collected as the calcite sample. Then all CO_2 evolved during the next 1.5 hours was discarded after measuring the yield in a manometer. After that the reaction vessel was placed into a boiling water bath for one hour, and the aliquot of CO_2 evolved was collected as the dolomite sample.

A sensitive method for measuring the amount of cross mixing is to use synthetic calcite-dolomite mixtures made of pure phases with different carbon isotope compositions. Here a calcite with $\delta^{13}C$ = -21.0‰ and dolomite with $\delta^{13}C$ = 3.5‰ were used. The results showed that using the procedure described above, only about 1.5% of calcite or dolomite was mixed with the other phase.

In medium and high grade metamorphic rocks typical of the Fennoscandian Shield, the differences in both the $\delta^{13}C$ values and in the $\delta^{18}O$ values of coexisting calcite and dolomite at equilibrium is expected to be below 1‰ (Sheppard & Schwarcz, 1970). However, the high temperature equilibrium between calcite and dolomite for oxygen in particular is generally not preserved, and for samples from the Fennoscandian Shield the difference in the $\delta^{18}O$ values of coexisting calcite and dolomite varies from -4 to 4‰ (Fig. 7).

To avoid cross-mixing calcite or dolomite in a mixture was analysed only, if its content was >15%. From this and the information presented above it may be calculated that the bias caused by cross-mixing can be expected to stay below about 0.1‰ for carbon isotopes and below about 0.4‰ for oxygen isotope ratios.

In addition to separate analysis of calcite and dolomite compositions, all mixed samples were also analysed separately for the isotope composition of total carbon by reacting the total carbonate at 100°C for one hour.

Analysis of sedimentary organic carbon

For the analysis of sedimentary organic carbon a weighed amount of rock powder was treated with concentrated HCl at 60°C for two hours in order to remove carbonate interferences, centrifuged and rinsed several times with distilled water, and finally dried at 90°C. Weight loss was determined and an aliquot of the acid residue was weighed into a 9 mm quartz tube together with 400 mg of CuO (e.g., Schoell et al., 1983). The tubes were evacuated and then sealed and heated at 950°C for two hours. The hot furnace and the samples were allowed to cool slowly over night.

The next day the CO_2 samples were purified in a vacuum line in the same way as the CO_2 samples extracted from carbonates. Any water or uncondensables were removed, and the sample was transferred to a manometer for the measurement of the yield.

The quartz tubing and CuO used for the reactions had been previously cleaned of organic contaminants by heating to 800°C for one hour. Under these conditions the CO_2 blanks were less than 0.5 µmole and insignificant relative to normal samples containing from 40 to 400 µmoles. In graphitic schists with abundant sulfides no traces of sulfur compounds could be detected in the mass spectrometer. Thirteen repeat analyses of a spectral carbon laboratory standard gave a $\delta^{13}C$ value of -18.00±0.03‰ (1SD). NBS-22 standard oil yielded a $\delta^{13}C$ value of -29.77‰, which may be compared to the $\delta^{13}C$ value of -29.61‰ reported by Coplen et al. (1983) and -29.81‰ suggested by Schoell et al. (1983).

Mass spectrometry

The carbon and oxygen isotope ratios of the CO_2 samples were determined using a Finnigan MAT 251 gas source mass spectrometer. All isotope values given in this work were calibrated using the international NBS-20 standard (Solenhofen limestone) and the isotope ratios given for it by Craig (1957).

PRESERVATION OF ORIGINAL ISOTOPE RATIOS

Following deposition sedimentary carbonates will be subjected to diagenetic modifications, where original micritic phases may be partly replaced by new, coarser grained mineral growth. Isotopic microanalyses of these newly formed phases have shown considerable variation caused by increasing temperature during burial, shifts in the oxygen isotope composition of the interstitial water and incorporation of diagenetically oxidated organic carbon in carbonate (e.g., Tucker, 1982; Hurley & Lohmann, 1989). In addition to microsampling, some control over these secondary changes in the original isotope ratios may be obtained from correlative variations in the trace element contents of carbonates (Veizer, 1983).

In this study no attempt was made to assess the extent of alteration by trace elements. Also, since metamorphic recrystallization has completely obliterated original diagenetic features in all Svecofennian and in many Karelian carbonates, only bulk carbonate compositions were determined.

During high grade metamorphism the original carbon isotope compositions of carbonates may be affected. One potential process is carbon exchange between carbonate and graphite, which can begin at temperatures as low as 350°C (Valley and O'Neil, 1981). However, for this work only relatively pure carbonate rocks

were collected, typically with very low graphite contents. On the basis of mass balance considerations the carbon isotope shift caused by exchange between carbonate and graphite may, therefore, be expected to be insignificant.

Another potential process causing lowering of original $\delta^{13}C$ values arises from metamorphic decarbonation reactions between carbonates and silicates. These reactions produce CO_2, which may escape from the system and that way affect the original isotope ratios. During metamorphism decarbonation typically leads to coupled ^{13}C and ^{18}O depletions (Valley, 1986). In this study the effects of decarbonation reactions should nevertheless be rather small, because generally only relatively pure carbonate rocks were analysed. In addition, no evidence of covariation can be observed between the $\delta^{13}C$ and $\delta^{18}O$ values on plots that include all isotopic data presented in this work (Figs. 6a and b).

Additional evidence suggesting only minor metamorphic shifts in the carbon isotope ratios of relatively pure carbonate rocks is provided by the systematic features of the $\delta^{13}C$ values presented in this study. For instance, in the Southern Svecofennian Province the metamorphic grade varies from amphibolite to granulite facies, but in spite of this the $\delta^{13}C$ values of sedimentary carbonates are tightly clustered between -0.8 and 1.2‰, while the $\delta^{18}O$ values vary more, ranging from 13.3 to 23.6‰ (Table 1). If the carbon isotope ratios had been significantly shifted by metamorphic processes, nearly constant $\delta^{13}C$ values could not be expected.

GENERAL RESULTS

Carbon and oxygen analytical results of the Paleoproterozoic sedimentary carbonates from the Fennoscandian Shield are given in Tables 1–10. In addition, these tables include the proportions of dolomite in the total carbonate fraction as determined by XRD analysis. Since the main aim of this work has been to study possible secular variations in the carbon isotope compositions of sedimentary carbonates, relevant litho- and chronostratigraphic information will also be reviewed.

The interpretation will be based on the $\delta^{13}C_{Tot}$ values, which for pure calcite or dolomite samples are identical to that of the analysed mineral compositions, but which for samples containing both calcite and dolomite were determined separately. In the following, a general overview of the whole data set will be given first, and then, in the following section, the individual schist areas will be treated in more detail.

Isotopic characteristics of the data

Figure 3 summarises the $^{13}C/^{12}C$ determinations presented in this work for the Paleoproterozoic sedimentary carbonates from the Fennoscandian Shield (Tables 1–10). The $\delta^{13}C_{Tot}$ values of carbonate range from about 16 to -4‰, with one outlier at -12‰. The distribution is bimodal, and there are strong maxima at about 1‰ and about 10‰. The former is similar to normal sedimentary carbonates, but the latter represents carbonates highly enriched in ^{13}C relative to average carbonates in the sedimentary record.

Sedimentary carbonates showing $\delta^{13}C$ values around 1‰ are found in all Paleoproterozoic supracrustal sequences throughout the Fennoscandian Shield. On the other hand, the sedimentary carbonates with $\delta^{13}C_{Tot} > 4‰$ are restricted to the supracrustal belts within the

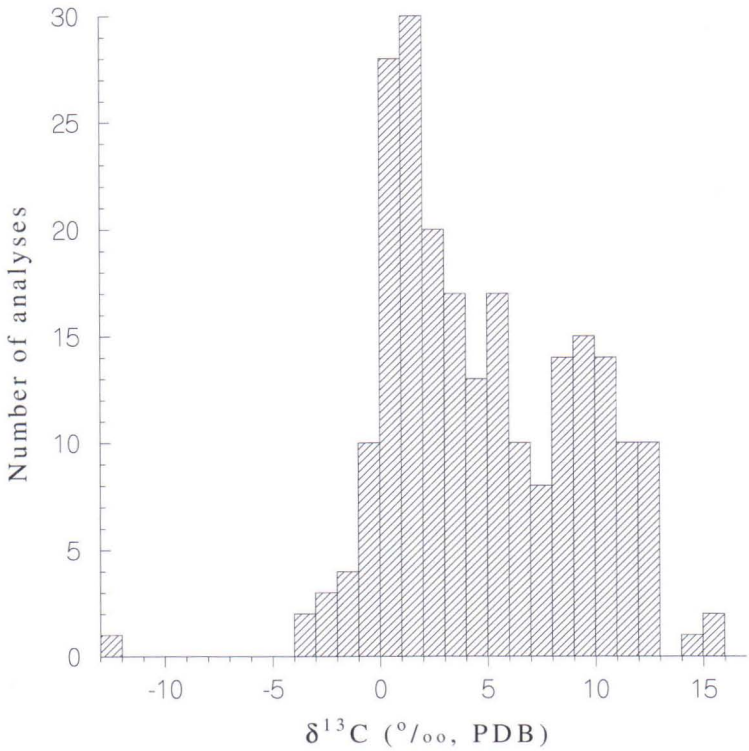

Fig. 3. Histogram of $\delta^{13}C_{Tot}$ values of sedimentary carbonates from the Fennoscandian Shield. The 229 carbonate analyses presented in this work show a bimodal distribution with one maximum at about 1 ‰ and another at about 10 ‰.

Archean Domain covering an area of about 1200x600 km^2 (Fig. 4). In fact, the western limit of these carbonates almost coincides with the western margin of the Archean craton inferred from the works of Koistinen (1981) and Öhlander et al. (1987).

Mineralogic characteristics of the data

Mineralogically the Paleoproterozoic sedimentary carbonate samples analysed in this study are predominantly either pure dolostones or pure limestones (Fig. 5). This strongly bimodal distribution resembles the pattern which has been found in the MgO/CaO ratios of sedimentary carbonate rocks from the Fennoscandian Shield (Pekkala, 1988). A similar, albeit less well-defined distribution in the percentage of dolomite has also been reported for Phanerozoic sedimentary carbonates from North America by Sperber et al. (1984). They noticed a pronounced maximum at 97% dolomite (dolostones) and another less distinct maximum at 20% (dolomitic limestones). Because similar bimodal distributions characterize most published data on Phanerozoic carbonates, Sperber et al. (1984) suggested that two separate processes may lead to these distinct populations. According to them, dolomitic limestones originated in diagenetically closed system during high-Mg calcite dissolution, and dolostones, on the other hand, are considered to have originated in diagenetically open systems

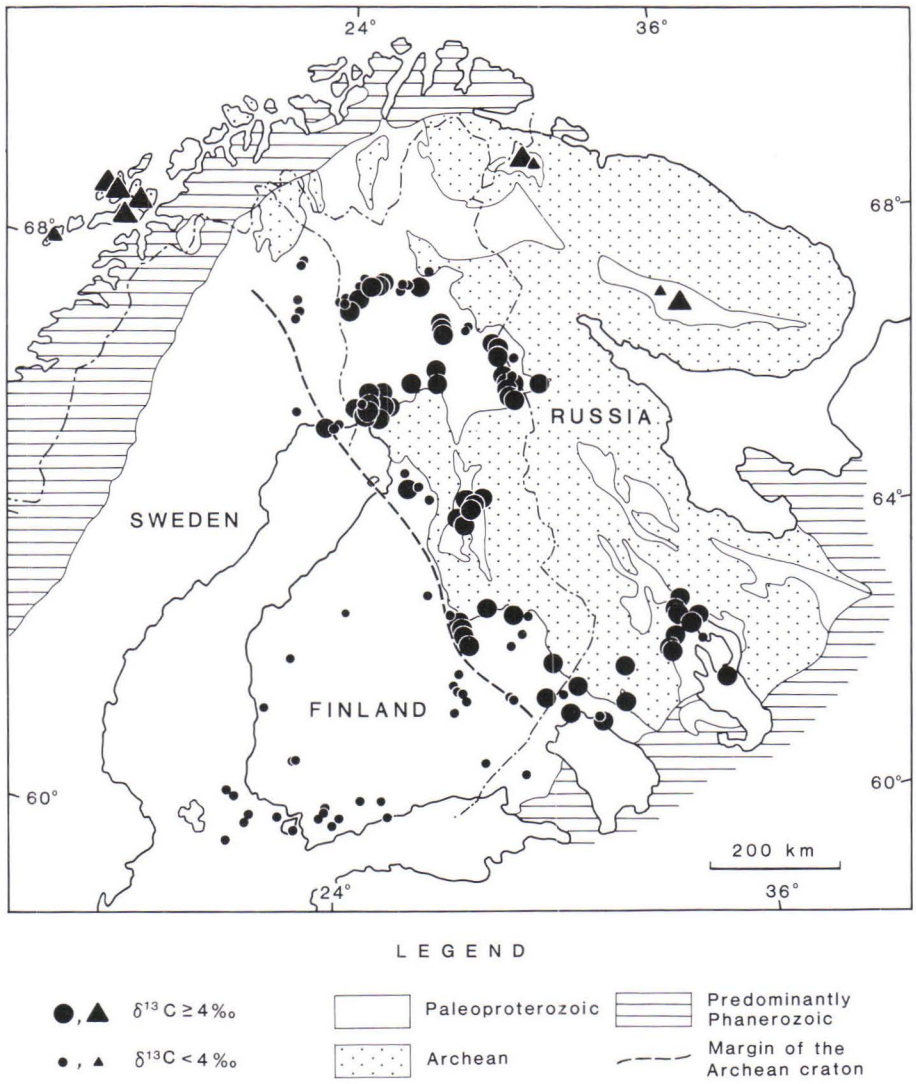

Fig. 4. Areal distribution of ^{13}C-enriched, Paleoproterozoic sedimentary carbonates in the Fennoscandian Shield. Circles designate analytical results from this work, triangles refer to published results of Karhu & Melezhik (1992) from the Pechenga and Imandra–Varzuga belts in Russia and of Baker & Fallick (1989b) from the Lofoten-Vesterålen area in Norway. The southwestern margin of the Archean craton is inferred from Koistinen (1981) and Öhlander et al. (1987). Sedimentary carbonates with $\delta^{13}C_{Tot}$ exceeding 4‰ are confined to supracrustal belts deposited on the Archean craton.

in the presence of an allochthonous Mg^{2+} supply. However, some Precambrian dolostones may be primary precipitates from seawater (Tucker, 1982), which might be another process, in addition to open system diagenesis, leading to essentially pure dolostones.

Although the data set is bimodal with respect to the $\delta^{13}C_{Tot}$ values and dolomite-calcite ratios, there is no clear correlation between the two variables. Figure 6a illustrates the $\delta^{13}C$ and $\delta^{18}O$ determinations for calcite and Figure 6b for dolomite. Both minerals define roughly

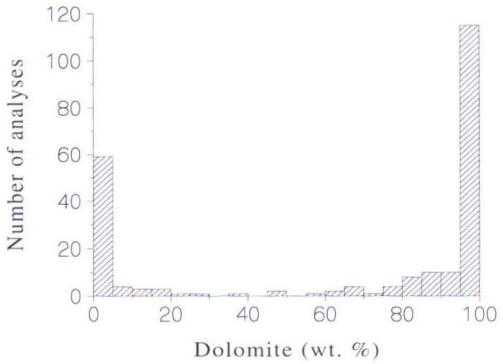

Fig. 5. Distribution of dolomite contents in total carbonate fraction of the Paleoproterozoic sedimentary carbonates from the Fennoscandian Shield, determined by XRD and the calibration curve shown in Figure 2. In hand specimen the majority of the 229 sedimentary carbonates analysed are nearly pure calcite or dolomite rocks.

similar fields in the $\delta^{13}C$ vs. $\delta^{18}O$ diagram, even though there is a general tendency for dolomite analyses to be concentrated towards higher $\delta^{13}C$ values than for calcite analyses. This is, however, easy to understand on the basis of the geographic distribution of the $\delta^{13}C$ values (Fig. 4) and on the old work of Eskola et al. (1919). They demonstrated that the sedimentary carbonate rocks of the Karelian formations are largely dolomitic, while the Svecofennian carbonate rocks are generally calcitic.

Figure 7 gives some information about the preservation of metamorphic equilibrium in coexisting calcite-dolomite pairs. The $\Delta^{13}C$ value refers to the difference in the $\delta^{13}C$ values of dolomite and calcite, and the $\Delta^{18}O$ values refer similarly to $\delta^{18}O$ values. The fields outlined in the diagram (Fig. 7) show the areas where dolomite and calcite are in metamorphic equilibrium in the temperature interval from 400 to 700°C. With respect to carbon the calcite-dolomite pairs are in near equilibrium, but in contrast, the $\delta^{18}O$ values show strong disequilibrium. In fact the majority of the calcite-dolomite pairs show inverse fractionation, the $\delta^{18}O$ values for dolomite generally being lower than those for calcite. Sheppard & Schwarcz (1970) noticed similar disequilibrium effects between

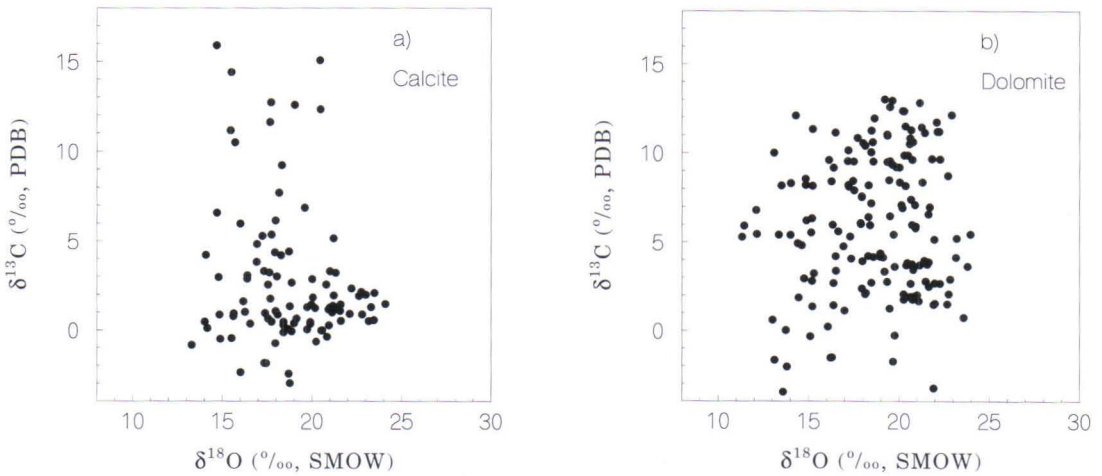

Fig. 6. Relationship between the $\delta^{18}O$ and the $\delta^{13}C$ values of 99 calcite analyses (a) and 164 dolomite analyses (b) for the Paleoproterozoic sedimentary carbonates from the Fennoscandian Shield. The plot includes all data from both pure calcite and dolomite rocks and from mixed calcite-dolomite rocks.

coexisting calcite and dolomite in regions metamorphosed under high grade conditions. They also presented evidence suggesting that the observed oxygen isotope shift could have resulted from more rapid exchange of calcite with an aqueous fluid relative to dolomite.

The calcite-dolomite pairs analysed in this study represent, with a few exceptions, either the Svecofennian Domain or the Karelian schist belts close to the southwestern margin of the Archean Domain, and in these areas the supracrustal sequences have generally been metamorphosed under amphibolite facies conditions. At these temperatures calcite and dolomite can be expected to reach isotopic equilibrium at the scale of a hand specimen, and the pronounced disequilibrium of oxygen isotope compositions apparently has resulted from retrograde, postmetamorphic reactions with an external oxygen reservoir.

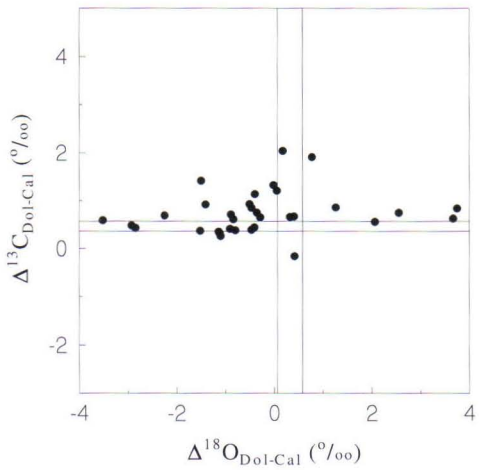

Fig. 7. Relationship between the $\Delta^{18}O$(Dolomite-Calcite) and the $\Delta^{13}C$(Dolomite-Calcite) values for 34 coexisting calcite-dolomite pairs. The narrow fields define areas where dolomite and calcite are in metamorphic equilibrium at 400–700°C with respect to isotopic composition of carbon or oxygen, following empirical calibrations of Sheppard & Schwarcz (1970).

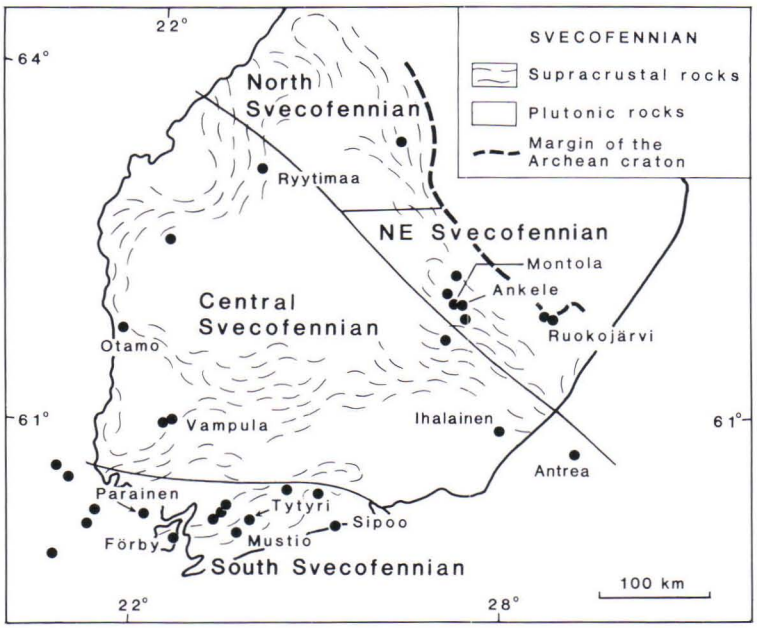

Fig. 8. Geological sketch map of the Svecofennian Domain showing sample locations. The Svecofennian provinces have been drawn largely after Gaál & Gorbatschev (1987), apart from the Northeast Svecofennian Province, which has been added on the basis of its distinct carbon isotope ratios.

Table 1. Carbon and oxygen isotope data for samples from the Svecofennian Domain.

Sample	Location	Dol[1]	$\delta^{13}C$, PDB[2]			$\delta^{18}O$, SMOW[2]	
		wt. %	Tot	Cal	Dol	Cal	Dol
South Svecofennian							
C-7	Parainen, quarry	0		0.28		18.40	
C-14	Rautsuo, Suomusjärvi	1		0.36		16.55	
C-67-A	Sipoo, quarry	0		0.04		19.72	
C-67-B	Sipoo, quarry	0		-0.01		20.57	
C-67-C	Sipoo, quarry	0		-0.02		20.53	
C-67-D	Sipoo, quarry	6		0.47		17.74	
C-67-E	Sipoo, quarry	87	-0.42	-0.74	-0.31	17.95	15.10
C-70-A	Parainen, quarry	0		0.47		14.02	
C-70-B	Parainen, quarry	1		0.27		20.95	
C-70-C	Parainen, quarry	1		0.45		19.90	
C-117	Förby, Särkisalo	0		0.35		19.90	
C-118	Mustio quarry	0		0.65		19.13	
C-119-A	Törmä, Lohja	0		0.46		18.41	
C-119-B	Solhem, Lohja	0		0.86		14.84	
C-119-C	Solhem, Lohja	0		0.65		17.55	
C-119-D	Solhem, Lohja	100			0.75		23.58
C-181	Kalkkivuori, Hyvinkää	0		0.39		19.00	
C-182	Kalkkivuori, Mäntsälä	0		0.06		18.67	
C-201	Kalkkimäki, Kiikala	0		-0.07		18.86	
C-202	Alskär, Korppoo	0		1.16		20.93	
C-204	Bergskär, Kökar	7	-0.15	-0.50		14.88	
C-205-A	Åvensor, Korppoo	11	-0.08	-0.13		18.40	
C-205-B	Åvensor, Korppoo	3		0.95		17.38	
C-206	Stenskär, Brändö	0		0.91		22.11	
C-207	Norra Härholm, Brändö	0		-0.46		15.51	
C-297	Toija, Kisko	0		-0.84		13.29	

1) Weight-% dolomite in total carbonate by XRD,
2) Tot = Total carbonate, Dol = Dolomite, Cal = Calcite.

$\delta^{13}C$ VARIATIONS IN STRATIGRAPHIC SECTIONS

Svecofennian Domain

Geologic setting

The Svecofennian Domain represents juvenile Paleoproterozoic formation of continental crust in the form of volcanic arcs, metagraywacke and metapelite dominated sedimentary basins and granitoid intrusions. The Svecofennian Domain was divided by Gaál & Gorbatschev (1987) into three provinces, which are the largely volcanogenic Northern and Southern Svecofennian provinces and the Central Svecofennian Province, which in addition to volcanic rocks is characterized by metagraywacke and metapelite dominated sedimentary belts. The province boundaries shown in Figure 8 are largely based on Gaál & Gorbatschev

Table 1. (continued)

Sample	Location	Dol[1]	$\delta^{13}C$, PDB[2]			$\delta^{18}O$, SMOW[2]	
		wt. %	Tot	Cal	Dol	Cal	Dol
Central Svecofennian							
C-65-A	Ihalainen, Lappeenranta	0		1.29		23.30	
C-65-B	Ihalainen, Lappeenranta	0		0.57		23.46	
C-65-C	Ihalainen, Lappeenranta	0		1.47		24.10	
C-66-B	Ryytimaa, Vimpeli	96	1.52		1.55		21.99
C-66-C	Ryytimaa, Vimpeli	3		0.51		23.17	
C-69	Kurikka	3		1.21		21.21	
C-122-A	Otamo, Siikainen	97	2.03		2.08		22.76
C-122-C	Otamo, Siikainen	94	1.35		1.51		22.68
C-123-B	Punola, Vampula	100			1.68		21.10
C-123-C	Punola, Vampula	0		1.08		21.57	
C-160	Kuparsaari, Antrea, Russia	1		1.23		20.18	
C-252	Hiirola, Mikkelin Mlk.	1		1.28		19.72	
C-290	Siivikkala, Vampula	10	0.93	0.88		22.80	
Northeast Svecofennian							
C-125-A	Ruokojärvi, Kerimäki	0		1.99		23.01	
C-125-B	Ruokojärvi, Kerimäki	0		2.09		23.49	
C-132-A	Ankele, Virtasalmi	59	1.86	0.87	2.08	18.08	18.13
C-132-B	Ankele, Virtasalmi	87	2.17	1.06	2.39	17.97	17.95
C-158	Mattilanmäki, Kerimäki	69	3.31	3.01	3.38	18.04	16.52
C-168	Montola, Virtasalmi	99	1.89		1.87		14.46
C-273	Rummukka, Jäppilä	86	1.68	1.36	1.77	21.17	20.26
C-292-1	Tutunen, Juva	0		2.86		20.08	
C-292-4	Tutunen, Juva	1		1.83		20.05	
C-366	Karsikumpu, Virtasalmi	0		1.44		21.60	
North Svecofennian							
C-293-2	Savijärvi, Pielavesi	1	-2.99	-2.99		18.76	
C-293-3	Savijärvi, Pielavesi	2	-2.36	-2.45		18.69	
C-316	Prästhom, Luleå, Sweden	49	-0.51	-0.65	-0.26	20.23	19.76

1) Weight-% dolomite in total carbonate by XRD,
2) Tot = Total carbonate, Dol = Dolomite, Cal = Calcite.

(1987), except that the lithologically and isotopically distinct northeastern corner of the Central Svecofennian Province has been separately distinguished here as the Northeastern Svecofennian Province. Samples were collected only from relatively large carbonate bodies, mostly from marble quarries.

$\delta^{13}C$ results

The $\delta^{13}C_{Tot}$ values of the Svecofennian sedimentary carbonates range from -3 to 3.5‰ (Table 1). They are, therefore, similar to normal sedimentary carbonates and also similar to Paleoproterozoic carbonates reported by Veiz-

er et al. (1992a, 1992b).

Although the carbon isotope compositions of the Svecofennian Domain show only limited variation, there are systematic differences between the various Svecofennian provinces (Fig. 9). The mean $\delta^{13}C_{Tot}$ values are 0.3±0.5‰ (1SD) for the southern province, 1.2±0.4‰ for the central province, 2.1±0.6‰ for the northeastern province and -2.0±1.3‰ for the northern province. Excluding the northern province, which has only three data points, there appears to be a general trend of decreasing $\delta^{13}C$ values with increasing distance from the Archean craton.

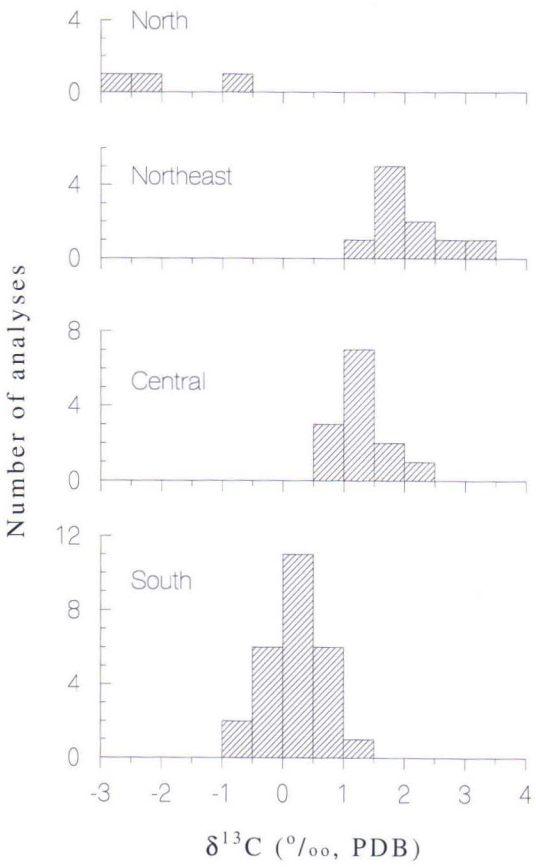

Fig. 9. Histogram of the $\delta^{13}C_{Tot}$ values of sedimentary carbonates from four provinces of the Svecofennian Domain.

Age constraints

Sedimentary carbonate formations of the Svecofennian Domain are associated with volcanogenic rocks, metagraywackes and mica schists, which provide some information about the age of deposition of these carbonates. The reported ages of volcanic rocks range from 1.87 to 1.91 Ga (Kähkönen et al., 1989; Vaasjoki & Lahti, 1991), while a minimum age for the deposition of the Svecofennian carbonates is provided by the 1.90 to 1.88 Ga intrusions of synorogenic granitoids.

A further constraint is set by metagraywackes in the Tampere region, lying below the volcanics in the stratigraphic sequence (Simonen, 1953). On the basis of ion microprobe U-Pb analyses on detrital zircons, they are constrained to have been deposited between about 1.93 and 1.90 Ga (Huhma et al., 1991).

Kiihtelysvaara–Onega region

Geologic setting

The sedimentary sequences in the Lake Onega, Suojärvi, Tulomozero and Soanlahti–Kiihtelysvaara areas (Fig. 10) represent Paleoproterozoic, epicontinental sedimentation on the Archean craton. Although these sequences are now present in isolated supracrustal belts within the Archean craton, they do show generally similar sedimentary successions, and they have been lithologically correlated (Sokolov, 1980, 1987).

The Paleoproterozoic formations in the Onega and Suojärvi areas include the classical outcrops where the traditional stratigraphic terms were first defined at the beginning of the 20th century (Ramsay, 1902, 1906; Metzger, 1924; Eskola, 1925). Current reviews describ-

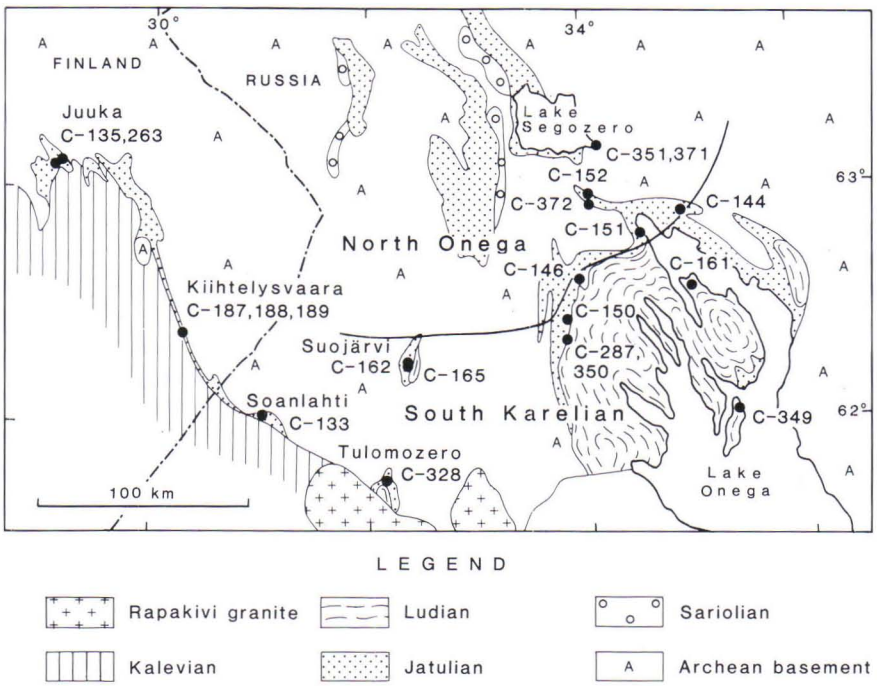

Fig. 10. Geological sketch map and sample locations of the Kiihtelysvaara-Onega region in southern Karelia based largely upon information from Gorbunov & Papunen (1985) and Sokolov (1980). The South Karelian and North Onega subprovinces are delineated after Sokolov (1980).

ing the Paleoproterozoic successions in this area are given by Sokolov (1980, 1987), Galdobina & Melezhik (1986), Gaskelberg et al. (1986) and Negrutsa et al. (1986). The Kiihtelysvaara area in eastern Finland has been studied by Nykänen (1971), Pekkarinen (1979) and Pekkarinen & Lukkarinen (1991).

The Sariolian (or Sumi-Sariolian) formations are present locally (Kohonen & Marmo, 1992; Pekkarinen & Lukkarinen, 1991; Gaskelberg et al., 1986). These formations are mostly coarse clastic graben fillings and do not contain sedimentary carbonates.

The weathering crust developed at the top of the Sariolian formations is overlain by metasediments of the Jatulian group, which in general represents an epicontinental transgressive sequence deposited on the Archean craton. Sokolov (1980) divided these successions into four areas or subprovinces with different types of Jatulian sequences. Two of them lie in the southern part of Russian Karelia, namely the South Karelian and the North Onega subprovinces (Fig. 10).

The Jatulian successions are overlain conformably by the Ludian supracrustal formations. In the South Karelian Subprovince the thickness of the Ludian may exceed 1 km, but in the North Onega Subprovince it is present only locally (Sokolov, 1980). Kohonen & Marmo (1992) have noted a similar north-south polarity between the Koli and the Kiihtelysvaara areas in Finland; in the latter, for instance, both the upper Jatulian dolostones and Ludian carbonaceous schist are present, while they are both absent from the former. They suggested that the supracrustal sequences preserved in these areas represent partly distinct stratigraphic levels. Evidently, this may also apply to successions in Russian Karelia.

The boundary between the Jatulian and the Ludian is marked by a sharp facies change from

Table 2. Carbon and oxygen isotope data for samples from the southern part of Russian Karelia.

Sample	Location	Dol[1]	$\delta^{13}C$, PDB[2]			$\delta^{18}O$, SMOW[2]	
	(stromatolite zone)	wt. %	Tot	Cal	Dol	Cal	Dol
North Onega Subprovince, Jatulian							
C-144	Voljärvi	100			12.58		19.50
C-151	Perguba	100			10.83		20.62
C-152	Ahvenjärvi	3		15.91		14.68	
C-351	Segozero	100			12.13		22.92
C-371	Segozero	100			11.73		22.09-
C-372	Tsobine	2		14.40		15.50	
South Karelian Subprovince							
Onega basin, Jatulian							
C-146	Tiudia	100			8.37		20.04
C-150	Suununjärvi	100			9.20		20.02
C-287-A	Raiguba *(Sundosia)*	100			9.53		18.58
C-287-B	Raiguba *(Nuclephyton)*	100			11.04		19.35
C-349-A	S. Oleny Island *(Butinella)*	100			9.67		21.83
C-349-B	S. Oleny Island *(Butinella)*	100			9.65		22.28
C-350	Raiguba *(Sundosia)*	100			8.73		22.72
Onega basin, Ludian							
C-161	Shunga	100			-3.24		21.92
Suojärvi, Jatulian							
C-162	Syväjärvi	100			10.62		20.77
C-165	Varpakylä *(Omachtenia)*	100			9.51		19.36
Tulomozero, Jatulian							
C-328-1	Lower Jatulian	100			11.50		20.35
C-328-2	Lower Jatulian	98			10.51		20.59
C-328-3	Upper Jatulian	100			9.61		16.13
C-328-4	Upper Jatulian	100			5.97		18.40
C-328-5	Upper Jatulian	100			7.92		17.52
Tulomozero, Ludian							
C-328-6	*Middle Ludian*	95	7.23		7.58		17.94
Soanlahti, Jatulian							
C-133	Kintsinniemi	100			8.37		21.31

1) Weight-% dolomite in total carbonate by XRD,
2) Tot = Total carbonate, Dol = Dolomite, Cal = Calcite.

light and red colored psammites and dolomites to gray and green colored, often carbonaceous schists and carbonate rocks (Sokolov, 1980). Also typical of the Ludian formations are intercalations of pyroclastic material and beds of carbonaceous schists, locally called shungites, in which the organic carbon content may attain 80%. The lower, so-called Trans-Onegian (Zaonezhye) formations of the Ludian group are overlain by the largely volcanogenic Suisaarian

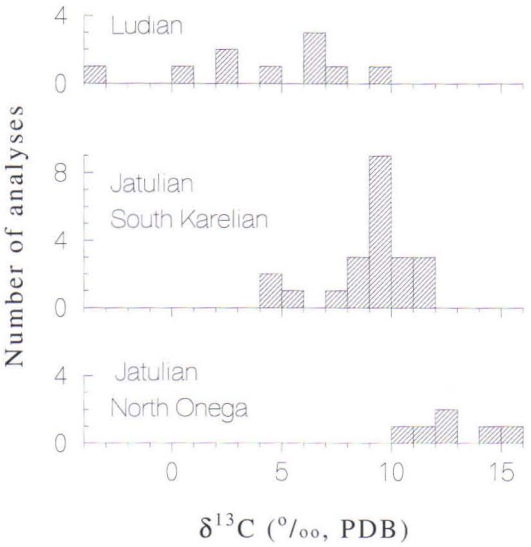

Fig. 11. Histogram of the $\delta^{13}C_{Tot}$ values of Ludian and Jatulian sedimentary carbonates from the South Karelian and the North Onega subprovinces of the Kiihtelysvaara–Onega region.

formations, which include the well-known ultramafic metalavas (Sokolov, 1980; Galdobina & Melezhik, 1986).

The sedimentary carbonate samples mostly represent Jatulian formations, although a few Ludian carbonate rocks have also been analysed. Since the term Ludian has not been applied to geologic formations in eastern Finland, the geology of the Kiihtelysvaara and Juuka areas (Fig. 10) will be discussed shortly below.

The stratigraphic succession in the Kiihtelysvaara area has been studied by Pekkarinen (1979) and Pekkarinen & Lukkarinen (1991). Based on their descriptions the Jatulian-Ludian transition is here placed between the Annala and Petäikkö formations. The Annala Formation consists of quartzite and hematite rock, and the overlying Petäikkö Formation comprises carbonate rocks, graphitic schists and phyllites. The lowermost beds of the Petäikkö Formation are variously pink and green, fine-grained dolomites (Pekkarinen, 1979), which may be regarded as a transitional sequence between the Jatulian and Ludian groups.

No comparable investigations have as yet been carried out in the Juuka district. Drill core samples (C-135-A, B; Table 3) from Petrovaara, Juuka, are impure carbonate rocks interlayered with graphitic schists and mica schists. The specimen (C-263) from the Polvela area represents a similar rock association, in which the graphitic schists have even been evaluated as a potential source of industrial graphite (Sarapää, 1988). Judging from the associated graphite bearing lithologies the Juuka samples may therefore be tentatively correlated with the Ludian group.

$\delta^{13}C$ results

The dolomite contents in the total carbonate fraction and the results of the isotopic analyses are given in Tables 2 and 3. The Jatulian sedimentary carbonates are with few exceptions pure or almost pure dolostones, whereas the dolomite-calcite ratios of the Ludian samples are variable.

The $\delta^{13}C$ values of total carbonate for Ludian samples and for Jatulian samples from the South Karelian and the North Onega subprovinces are shown separately in Figure 11. All Jatulian sedimentary carbonates from this area are highly enriched in ^{13}C, with $\delta^{13}C_{Tot}$ values from 6.0 to 15.9‰, and this is especially true for the North Onega Subprovince, in which the $\delta^{13}C_{Tot}$ values range from 10.8 to 15.9‰. In contrast, the $\delta^{13}C_{Tot}$ values of sedimentary carbonate samples from Ludian formations are highly variable and range from enriched compositions of 9.4 down to -3.2‰. These regularities in the distribution of carbon isotope compositions will be investigated in more detail below.

Stratigraphic $\delta^{13}C$ variations

Figures 12, 13 and 14 show $\delta^{13}C_{Tot}$ results of sedimentary carbonates against their positions in the sedimentary column for the Kiihtelys-

Table 3. Carbon and oxygen isotope data for samples from the Kiihtelysvaara and Juuka areas.

Sample	Location	Dol[1]	$\delta^{13}C$, PDB[2]			$\delta^{18}O$, SMOW[2]	
	Drill core/Depth (m)	wt. %	Tot	Cal	Dol	Cal	Dol
Kiihtelysvaara, Viistola Formation, Jatulian							
C-187-D	R309/66.4	100			9.88		20.29
C-187-A	R309/64.5	100			11.20		22.23
C-187-B	R309/54.5	99			10.05		18.46
C-188-B	R310/174.6	97	9.45		9.55		19.51
C-188-C	R310/164.3	99			9.55		17.17
C-188-J	R310/149.7	0		4.82		16.93	
C-188-E	R310/135.6	7	4.25	4.19		18.27	
Kiihtelysvaara, Petäikkö Formation, Ludian							
C-188-K	R310/109.9	48	6.53	6.14	6.98	17.97	21.71
C-188-H	R310/82.6	99			6.03		17.89
C-189-A	R311/170.4	16	0.90	0.78	2.69	15.61	16.38
C-189-F	R311/123.5	4	2.94	3.07		16.39	
C-189-J	R311/105.4	2	2.88	2.88		16.38	
Juuka							
C-135-A	Petrovaara	77	6.26	5.97	6.35	16.00	15.20
C-135-B	Petrovaara	84	4.78	4.35	4.94	17.93	14.41
C-263	Polvela	99			9.36		19.63

1) Weight-% dolomite in total carbonate by XRD,
2) Tot = Total carbonate, Dol = Dolomite, Cal = Calcite.

vaara, Tulomozero and Central Onega areas, respectively.

The Kiihtelysvaara column (Fig. 12) represents the Viistola composite drill core section described by Pekkarinen (1979). The generalized stratigraphic column and the lithostratigraphic names are here given after Pekkarinen & Lukkarinen (1991). The $\delta^{13}C_{Tot}$ values of sedimentary carbonates in the Kiihtelysvaara section show a decreasing trend from about 10 down to about 2‰. The shift from ^{13}C-enriched carbonates down to normal sedimentary carbonates is not linear, but appears to show a cyclic pattern superimposed on the general trend. For instance, immediately below the Annala Hematite Formation there is a local minimum at a $\delta^{13}C_{Tot}$ value of about 4‰.

The Tulomozero section (Fig. 13) is more qualitative in nature. Traversing upwards from the Archean basement the first two dolomite samples have been collected from the lowest part of the stratigraphic succession. The next three samples were taken from a drill core intersecting hematite-bearing layers about 40 m below the Jatulian–Ludian transition. The uppermost Ludian dolomite sample represents sedimentary carbonates in the middle part of the Ludian group, about 200 m above the Jatulian-Ludian contact.

As in the Kiihtelysvaara section the Tulomozero samples show a decreasing $\delta^{13}C_{Tot}$ trend commencing at about 11‰ and ending at about 8‰ in the Ludian. In addition there appears to be a sharp local minimum associated with the hematite layer, in which the $\delta^{13}C$ goes down to about 6‰.

The stratigraphic positions of the samples from the Lake Onega area are not very well constrained. However, since sedimentary carbonates in that area commonly contain stroma-

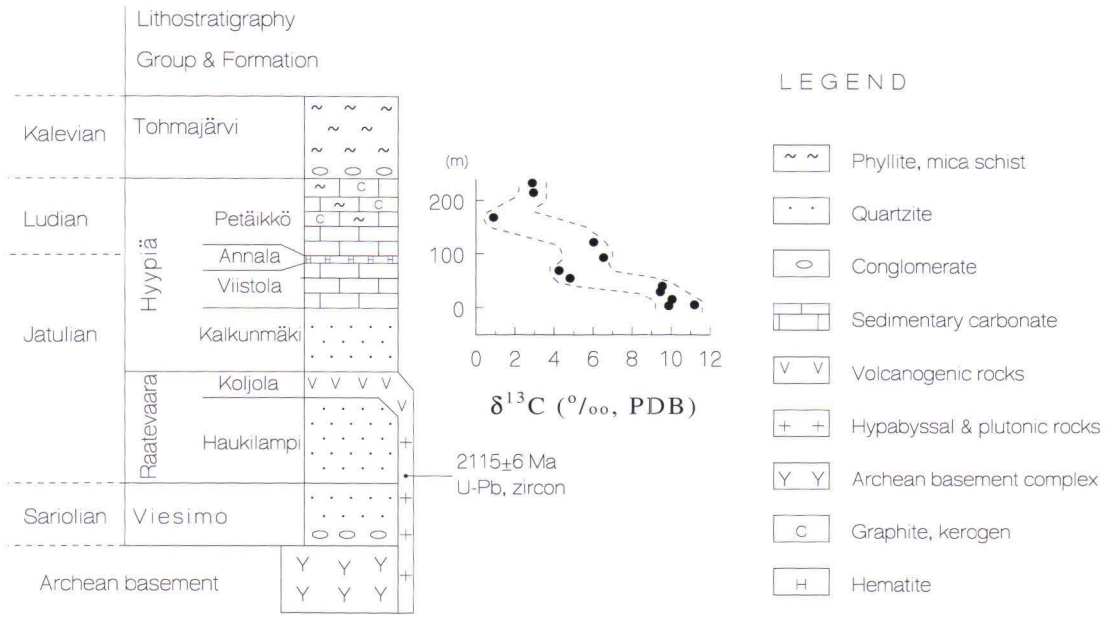

Fig. 12. Lithostratigraphic column of the Kiihtelysvaara area after Pekkarinen & Lukkarinen (1991) and the variation of the $\delta^{13}C_{Tot}$ values of sedimentary carbonates in the drilling profile R309-310-311 across the Hyypiä Group. The profile has been described by Pekkarinen (1979).

tolitic structures, an attempt was made to study the $\delta^{13}C$ variations by stromatolite biostratigraphy, which is based on the morphology of certain stromatolite groups and forms (Krylov, 1976; Semikhatov, 1976).

An extensive study of stromatolites in eastern Karelia has been published by Makarikhin & Kononova (1983) and later reviewed by Makarikhin (1992). The partial stratigraphic column in Figure 14 has been constructed from their data, and includes those dolomite samples from the central Onega area of the South Karelian Subprovince that either contain identified stromatolite structures or have been collected from beds containing identified stromatolite groups and forms. The specimen (C-165) from the *Omachtenia kintsiensis* bearing zone has been classified on the basis of a columnar stromatolite form *Carelozoon jatulicum* (see Makarikhin & Kononova, 1983, Fig. 66; Makarikhin, 1992). The Ludian sample is only shown for comparison, and it is not known to contain stromatolites.

The stromatolite form *Carelozoon jatulicum* was originally described by Metzger (1924) from erratic boulders found in the vicinity of Lake Suojärvi. Later this stromatolite form has been identified in situ both from Lake Suojärvi and Lake Onega, where it forms an important

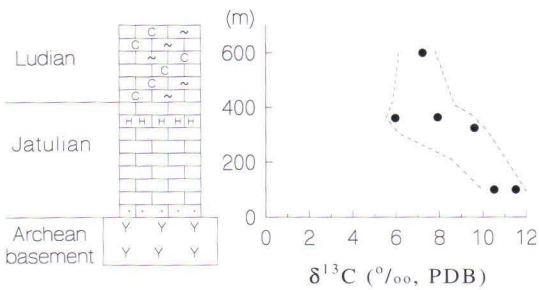

Fig. 13. Generalized stratigraphic column of the Tulomozero area based on information in Sokolov (1980) showing the variation of the $\delta^{13}C_{Tot}$ values of dolomites from different levels in the stratigraphic column. Symbols as in Fig. 12.

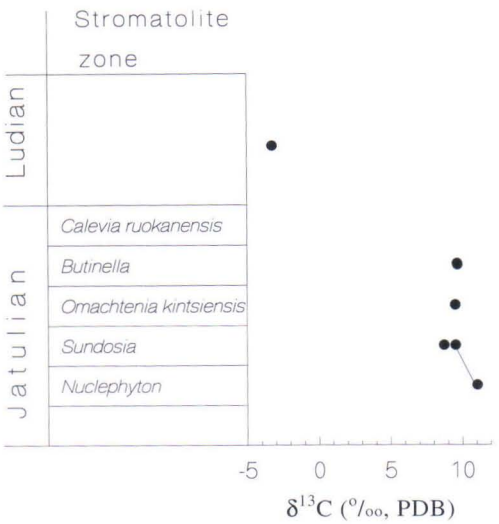

Fig. 14. Variation of the $\delta^{13}C_{Tot}$ values of stromatolitic dolomites from the South Karelian Subprovince. The stratigraphical order of the samples is based only on stromatolite biostratigraphic data in Makarikhin & Kononova (1983) and Makarikhin (1992), except for the two samples connected by a tie line, which have been collected from the same outcrop.

correlation horizon (Sokolov, 1980; Makarikhin & Kononova, 1983). The isotopic analysis of *Carelozoon jatulicum* (C-165) was made from an original specimen collected and described by Metzger (1924).

The stromatolitic dolomites from the South Karelian Subprovince show nearly constant $\delta^{13}C_{Tot}$ values within the range 9.9±1.1‰. The $\delta^{13}C_{Tot}$ value of the Ludian dolomite sample is -3.2‰, which indicates a significant shift from the Jatulian isotope pattern (Fig. 14).

The stratigraphic successions in the Lake Onega, Tulomozero and Kiihtelysvaara districts have been correlated lithologically with each other (Pekkarinen, 1979; Sokolov, 1987). In addition, the $^{13}C/^{12}C$ ratios of carbonate in each of these supracrustal belts show similar evolutionary trends from highly ^{13}C enriched carbon in the Jatulian to lower and variable $\delta^{13}C$ values in the Ludian.

Age constraints

At Kiihtelysvaara a diabase dike terminating at the volcanic Koljola Formation and presumably representing a feeder for the lava flow has an age of 2115±6 Ma (Pekkarinen & Lukkarinen, 1991). This indicates that all sedimentary carbonates in the Kiihtelysvaara area were deposited after this time (see Fig. 12). If the lithologic correlations presented by Sokolov (1987, Fig. 13) are correct, this applies also to other carbonate samples from the South Karelian Subprovince.

A gabbro intrusion from the Suisaarian formations in the upper part of the Ludian group has given a Sm-Nd mineral isochron age of 1980±27 Ma (Pukhtel' et al., 1992). This places a minimum age constrain on the Trans-Onegian (Zaonezhye; Sokolov, 1980) formations of the Ludian group.

It may therefore be concluded that the deposition of the highly ^{13}C-enriched sedimentary carbonates and the shift to normal sedimentary carbonates in the South Karelian Subprovince probably occurred between 2115 and 1980 Ma.

Pitkäranta and Kuopio areas

Geologic setting

The Pitkäranta and Kuopio areas lie at the western margin of the Archean craton, the former in the northern corner of Lake Ladoga in Russia and the latter in central Finland (Fig. 1). Characteristic of the geology of these two areas are Archean gneiss domes surrounded by a regular succession of supracrustal formations, which in both areas include sedimentary carbonates. These structures constitute some of the well known mantled gneiss domes discussed by Eskola (1949).

Pitkäranta. The Pitkäranta region is an old

mining area, and the area of eastern domes (Fig. 15) was thoroughly investigated and mapped in the course of mining operations by Trüstedt (1907). The geology and stratigraphy of the large sedimentary carbonate deposit of Ruskeala has been studied by Metzger (1925). More recent cross sections of the stratigraphic successions have been given by Galdobina (1987, Fig. 14).

Around the eastern domes of the Pitkäranta region (Fig. 15) the basement is overlain by a very regular rock sequence called here the Pitkäranta group (Pitkäranta suite, Galdobina & Melezhik, 1986). It starts with a 2–15 m thick continuous, sedimentary carbonate horizon, and is followed by 100–300 m of hornblende schists containing graphite and carbonate bearing interlayers, which in turn are overlain by a second carbonate horizon, 5–40 m in thickness (Trüstedt, 1907).

Around the western domes (Fig. 15) the sequence of the supracrustal rocks is more irregular and complicated. Sedimentary carbonate layers are discontinuous, and apparently occur at more than just two stratigraphic levels. Also, the thickness of the amphibole schist horizon is greater, approaching 1 km and, in addition, basaltic lavas occur (Galdobina, 1987). The Pitkäranta group is overlain by Ladogan mica schists, and has been correlated with the Ludian group (Sokolov, 1980; Galdobina & Melezhik, 1986; Galdobina, 1987).

Sedimentary carbonate samples were collected from the lower and upper carbonate horizons of the Pitkäranta group. In the area of the eastern domes there are no difficulties in assigning the samples to either the lower or the upper carbonate horizon. In the area of the western domes at Ruskeala Archean basement is not exposed (Fig.15) and also the stratigraphic succession is more complicated. However, the large carbonate deposit at Ruskeala lies between amphibole schist and mica schist just as the upper carbonate horizon in the area of the eastern domes, and based on this it appears to form a direct continuation of the upper carbonate horizon (Metzger, 1925).

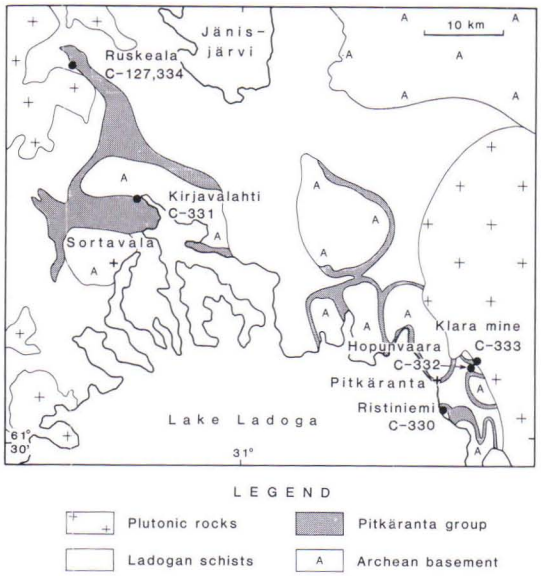

Fig. 15. Geological sketch map and the sample locations in the Pitkäranta area at the northern corner of the Lake Ladoga, Russia. The map is based on information in Trüstedt (1907) and Hackman (1933).

Kuopio. The supracrustal sequence surrounding the Archean gneiss domes of the Kuopio area has been described in detail by Wilkman (1923). Later studies were made by Eskola (1949) and Preston (1954), who, however, concentrated more on doming. Aumo (1983) described the stratigraphy of the Kuopio area and named the formations in the succession.

The stratigraphic sequence surrounding the Archean gneiss domes in the Kuopio area resembles the succession in the Pitkäranta area. However, the sequence at Kuopio differs in that it begins with siliciclastic metasediments, although their total thickness remains rather small, varying between 0 and 250 m (Aumo, 1983).

The siliciclastic metasediments are followed by pure and impure carbonate rocks and graphitic schists of the Petonen Formation, which are overlain by basic metalavas of the Vaivanen Formation.

Wilkman (1923) already noted that graphitic

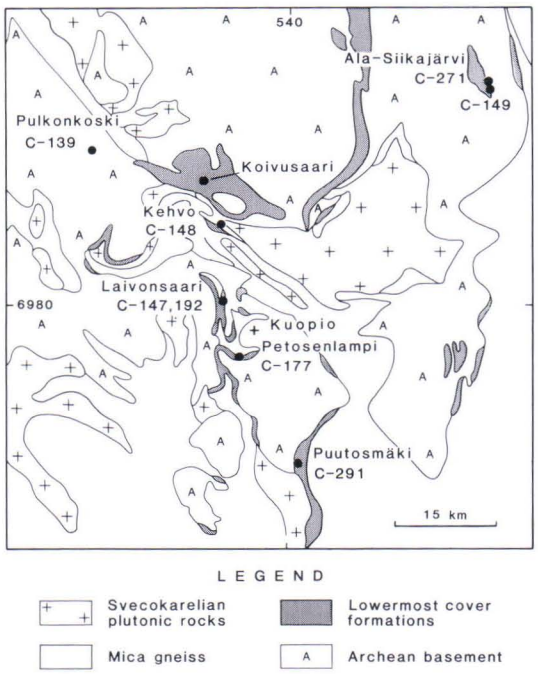

Fig. 16. Geological sketch map and the sample localities in the Kuopio and Ala-Siikajärvi areas mainly after Luukkonen & Lukkarinen (1985). Also shown is the site of the felsic volcanic rock sample (Koivusaari), which has yielded a U-Pb age of 2062±2 Ma (Pekkarinen & Lukkarinen, 1991).

schists occur within the sedimentary carbonate formation and especially in its lower part. The carbon content of the graphitic schists may even exceed 50%, and clearly these metasediments represent an environment with high burial rate of organic carbon, typical for supracrustal formations of the Ludian group. The volcanic Vaivanen Formation is followed by Kalevian turbiditic mica schists.

The sample locations are shown in Figure 16. At the Petosenlampi (C-177) and Laivonsaari (C-147, C-192) sites it was possible to collect two and three samples, respectively, in stratigraphic sequence. Most samples are clearly in a stratigraphic position below the mafic metalavas, but there is one dolomite occurrence (C-139, Pulkonkoski), surrounded exclusively by rocks of the basement complex. Therefore, the stratigraphic position of this sample is unclear.

Ala-Siikajärvi. Two samples were analysed from the Ala-Siikajärvi schist belt, which is a separate Karelian schist area enclosed within the Archean basement complex about 60 km northeast from Kuopio (Fig. 16). The stratigraphic succession in the Ala-Siikajärvi schist belt has been described by Grind (1988) and is similar to the sequence in the Kuopio area. However, in the Ala-Siikajärvi area sedimentary carbonates are additionally present among graphitic schists above a volcanogenic formation.

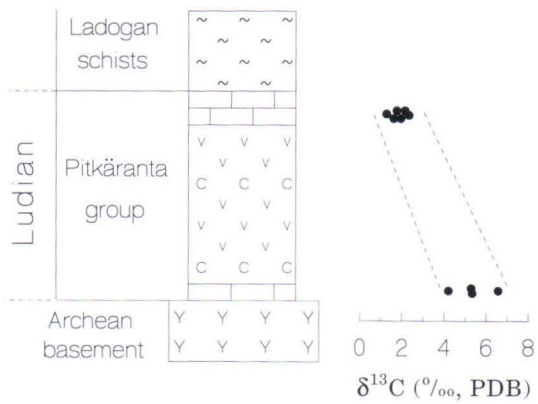

Fig. 17. Stratigraphic column of the Pitkäranta area after Trüstedt (1907) also showing the variation of the $\delta^{13}C_{Tot}$ values of sedimentary carbonates in the stratigraphic sequence. Symbols as in Fig. 12.

$\delta^{13}C$ results

The dolomite contents in the total carbonate fraction and the carbon and oxygen isotope data for the sedimentary carbonates from the Pitkäranta, Kuopio and Ala-Siikajärvi areas are given in Table 4. Generalized stratigraphic columns and variations of the $\delta^{13}C_{Tot}$ values in the stratigraphic columns are illustrated in Figure 17 for samples from the Pitkäranta area, in Figure 18 for samples from the Kuopio area and in Figure 19 for samples from the Ala-Siikajärvi schist belt.

Pitkäranta. In the Pitkäranta area the sedimentary carbonate samples from the lower carbonate horizon gave a mean $\delta^{13}C_{Tot}$ value of

Table 4. Carbon and oxygen isotope data for samples from the Pitkäranta area in Russia and Kuopio and Ala-Siikajärvi areas in Finland.

Sample	Location	Dol[1]	$\delta^{13}C$, PDB[2]			$\delta^{18}O$, SMOW[2]	
		wt. %	Tot	Cal	Dol	Cal	Dol
Pitkäranta area							
Upper Pitkäranta group							
C-127-A	Ruskeala quarry	0		2.34		22.21	
C-127-B	Ruskeala quarry	0		2.15		22.76	
C-332-A	Hopunvaara, Pitkäranta	1		1.27		21.01	
C-332-B	Hopunvaara, Pitkäranta	0		1.76		17.68	
C-333	Klara mine, Pitkäranta	63	1.40	1.00	1.93	21.13	20.62
C-334-A	Ruskeala quarry	0		1.61		16.17	
C-334-B	Ruskeala quarry	0		1.95		21.22	
Lower Pitkäranta group							
C-330-A	Ristiniemi, Pitkäranta area	1		4.21		14.08	
C-330-B	Ristiniemi, Pitkäranta area	1		6.58		14.70	
C-331-A	Kirjavalahti, Sortavala	96	5.30		5.41		14.01
C-331-B	Kirjavalahti, Sortavala	13	5.35	5.35	5.61	17.74	16.64
Kuopio area							
Unclassified							
C-139	Pulkonkoski, Siilijärvi	91	1.09		1.14		16.99
Petonen Formation							
C-147	Laivonsaari, Kuopio	83	5.86	5.28	5.99	17.23	16.34
C-148	Kehvo, Siilinjärvi	81	5.72	5.15	5.80	21.21	20.92
C-177-A	Petosenlampi, Kuopio	97	6.40		6.43		18.31
C-177-B	Petosenlampi, Kuopio	26	0.99	0.93	1.37	15.63	15.22
C-192-F	Laivonsaari, Kuopio	65	4.84	4.40	5.32	18.71	17.30
C-192-G	Laivonsaari, Kuopio	78	3.02	2.55	3.24	17.55	15.30
C-291	Puutosmäki, Vehmersalmi	89	5.93		6.09		17.88
Alasiikajärvi schist belt							
Upper carbonate formation							
C-149	Huttuniemi, Juankoski	89	1.44		1.44		16.38
Lower carbonate formation							
C-271	Huosiaisniemi, Juankoski	99	6.56		6.58		21.64

1) Weight-% dolomite in total carbonate by XRD,
2) Tot = Total carbonate, Dol = Dolomite, Cal = Calcite.

5.4±1.0‰, and those from the upper carbonate horizon a $\delta^{13}C_{Tot}$ value of 1.8±0.4‰. Consequently, there is a significant 3.6‰ drop in the $\delta^{13}C$ values from the lower to the upper carbonate horizon (Fig. 17).

Kuopio. Sedimentary carbonate samples from the Petonen Formation in the Kuopio area gave a mean $\delta^{13}C_{Tot}$ value of 4.7±2.0‰, which

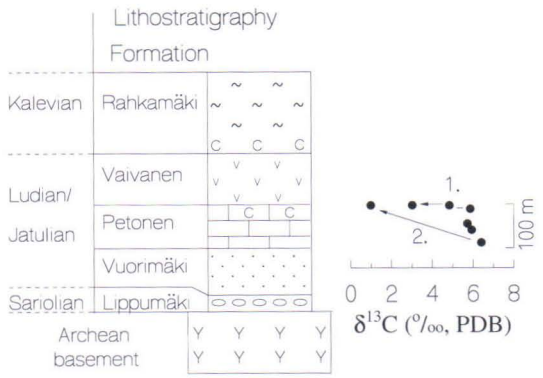

Fig. 18. Lithostratigraphy of the Kuopio area after Aumo (1983) and $\delta^{13}C_{Tot}$ values of sedimentary carbonates in the Petonen Formation. Tie lines connect samples from stratigraphic profiles at Laivonsaari (1) and at Petonen (2). Symbols as in Fig. 12.

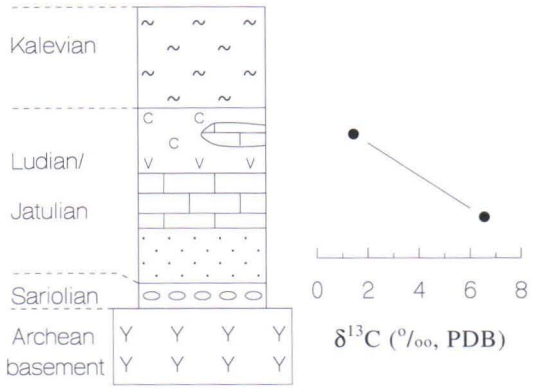

Fig. 19. Stratigraphic column for the Ala-Siikajärvi area drawn based on information in Grind (1988) and the $\delta^{13}C_{Tot}$ values of two sedimentary carbonate samples at different stratigraphic levels. Symbols as in Fig. 12.

is within error limits the same as the mean $\delta^{13}C_{Tot}$ value of the lower carbonate formation of the Pitkäranta group. In addition, $\delta^{13}C$ values appear to be decreasing towards the contact of the Vaivanen Formation, as is shown by the two sample profiles (Fig. 18).

Ala-Siikajärvi. Dolomite samples from the lower and upper carbonate formations of the Ala-Siikajärvi schist belt yielded $\delta^{13}C_{Tot}$ values of 6.6 and 1.4‰, respectively (Fig. 19), which are similar to the $^{13}C/^{12}C$ ratios of the corresponding formations of the Pitkäranta group.

Age constraints

A felsic ash-flow metatuff from the Koivusaari Formation in the Siilinjärvi area, north of Kuopio (see Fig. 16) has been dated to 2062±2 Ma using the U-Pb method on zircon (Pekkarinen & Lukkarinen, 1991). The Koivusaari Formation may correlate with the Vaivanen Formation of the Kuopio area, which has a similar stratigraphic context (Lukkarinen, 1990).

Kalevian provinces

At the western margin of the Archean craton the basement and the Jatulian and Ludian supracrustal units are overlain, often disconformably, by deeper water Kalevian mica schists (Simonen, 1980; Meriläinen, 1980). Although these metasediments were previously regarded as a single homogenous lithostratigraphic sequence, recent studies suggest that the Kalevian provinces represent more complex assemblages of sedimentary units deposited at different times possibly in different sedimentary basins (Ward, 1988). In addition, these provinces also seem to contain remnants of Jatulian and Ludian supracrustal successions, which is consistent with the carbon isotope results in this study.

Sedimentary carbonate samples were included from the Northern Ostrobothnia Schist Belt in northern Finland and from the North Karelian Schist Belt in eastern Finland (Fig. 1). In addition, the Kalevian metasediments of the Kainuu schist belt are also represented by one sample.

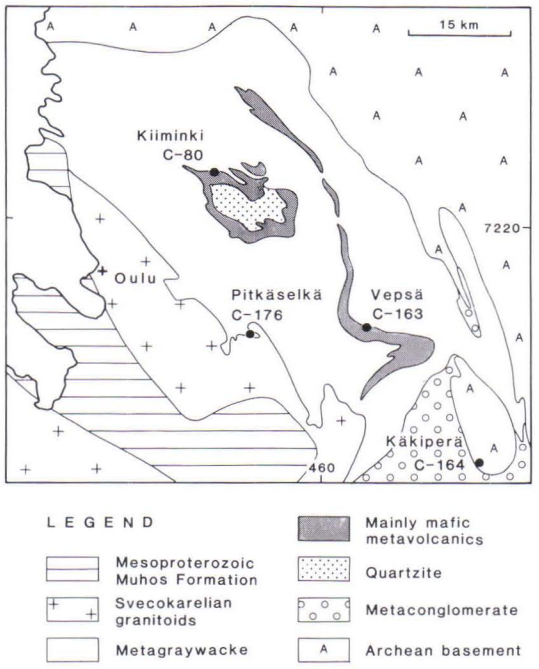

Fig. 20. Geological sketch map of the Northern Ostrobothnia Schist Belt according to information in Honkamo (1989), also showing locations of samples analysed in this study.

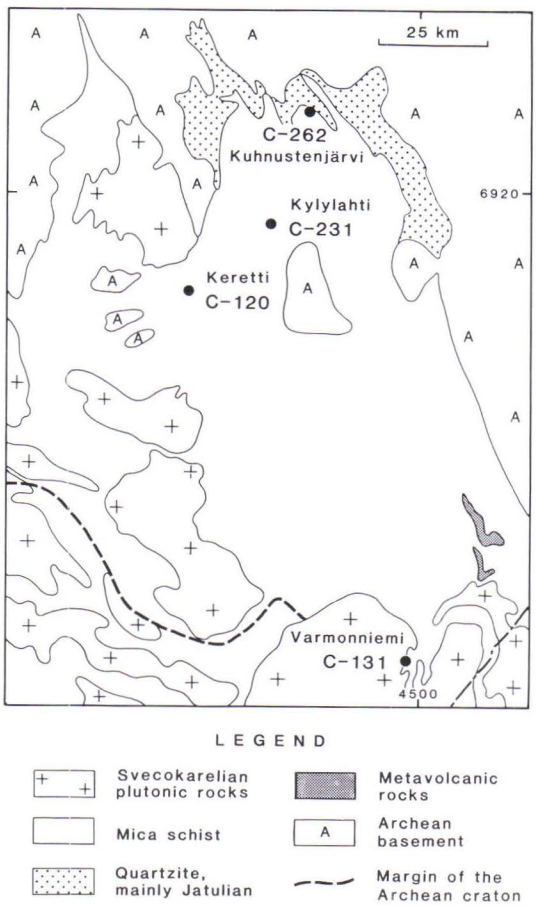

Fig. 21. Geological sketch map of the North Karelia Schist Belt based on Luukkonen & Lukkarinen (1985), also showing sample locations.

Geologic setting

Northern Ostrobothnia. The geology and stratigraphy of the Northern Ostrobothnia Schist Belt has been described by Honkamo (1985, 1988, 1989). The 5–8 km thick supracrustal sequence is dominated by metagraywackes (Fig. 20), which were generally deposited directly on the Archean basement. In the southeastern part of the belt the succession starts with massive conglomerates, which are replaced by metagraywackes higher up in the sequence. The lower metagraywackes are covered by formations containing mafic metavolcanics, quartzites and chemical sediments, which in turn are overlain by metagraywackes.

The sample locations of sedimentary carbonates are shown in Figure 20. Two samples (C-80, 163) have been collected from formations directly associated with mafic metavolcanic units between the metagraywacke successions. The carbonate sample from Käkiperä (C-164) is associated with metavolcanics and quartzites in an area dominated by rocks of the Archean basement complex (Honkamo, 1989). The Pitkäselkä dolomite (C-176) represents an association of quartzite and dolomite lying along the contact of Svecokarelian granitoids and the metagraywackes of the schist belt.

North Karelia. The geology of the North Karelia Schist Belt in eastern Finland has been extensively studied largely due to the economic potential of the Outokumpu Ore District. In these deposits massive Cu-Zn-Co orebodies are associated with an assemblage including serpentinites, calc-silicate rocks, metacherts and

Table 5. Carbon and oxygen isotope data for samples from the Kalevian successions.

Sample	Location	Dol[1]	$\delta^{13}C$, PDB[2]			$\delta^{18}O$, SMOW[2]	
		wt. %	Tot	Cal	Dol	Cal	Dol
Northern Ostrobothnia Schist Belt							
C-80	Kiiminki, quarry	94	0.16		0.23		16.07
C-163	Vepsä, Ylikiiminki	97	1.97		2.14		18.17
C-164	Käkiperä, Utajärvi	80	1.12		1.26		19.48
C-176	Pitkäselkä, Muhos	100			8.12		17.23
North Karelia Schist Belt							
C-131	Varmonniemi, Kesälahti	90	6.43		6.48		19.50
C-120-A	Keretti, Outokumpu	73	-1.55	-1.86	-1.51	17.44	16.30
C-120-B	Keretti, Outokumpu	85	-1.53	-1.85	-1.53	17.34	16.22
C-231-A	Kylylahti, Outokumpu	94	-3.60		-3.46		13.60
C-231-B	Kylylahti, Outokumpu	88	-2.35		-2.04		13.81
C-262	Kuhnustenjärvi, Juuka	100			2.69		21.98
Kainuu Schist Belt							
C-266	Talvivaara, Sotkamo	99			-12.47		13.27

1) Weight-% dolomite in total carbonate by XRD,
2) Tot = Total carbonate, Dol = Dolomite, Cal = Calcite.

black schists, known collectively as the Outokumpu Assemblage (Huhma & Huhma, 1970; Koistinen, 1981; Papunen, 1987). The ore deposits and associated rocks are enclosed in mica schists, which are the predominant rock type of the region.

The Kalevian metasediments of the area represent a diverse assemblage of autochthonous units and allochthonous thrust sheets and nappe complexes (Koistinen, 1981; Ward, 1988). The earliest sedimentary units may have been deposited already at 2105±15 Ma (Ward, 1988), which is based on a zircon age from the volcanic Tohmajärvi complex (Huhma, 1986). The latest mica schists are lying stratigraphically above the rocks of the Outokumpu Assemblage, and their depositional age is presumably younger than 1972±18 Ma (Koistinen, 1981).

Sample locations are shown in Figure 21. Four carbonate samples from two localities (C-120, 231) represent dolomite rocks of the Outokumpu Assemblage. According to current interpretations the carbonates, cherts and sulfides of the assemblage were deposited from hydrothermal fluids onto oceanic crust (Koistinen, 1981; Papunen, 1987), and, therefore, the carbon isotope ratios of these carbonates may have been affected by hydrothermal input.

The dolomite sample from Kuhnustenjärvi (C-262) has been collected from a conglomerate with carbonate clasts in a mica schist environment. The sedimentary carbonate occurrence at Varmonniemi (C-131) is located in a narrow remnant of schists within a Svecokarelian granite pluton (Fig. 21), and is associated with amphibole and graphite bearing schists and quartzite (Nykänen, 1975).

$\delta^{13}C$ results

Results of isotopic analyses and the dolomite contents of the sedimentary carbonate samples from the Kalevian provinces are given in Table 5. The $\delta^{13}C_{Tot}$ values range from -12.5 to 8.1‰, and thus the sedimentary carbonates

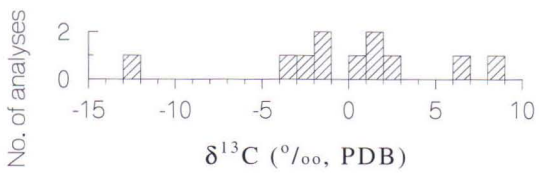

Fig. 22. Histogram showing the $\delta^{13}C_{Tot}$ values of the sedimentary carbonates from the Kalevian provinces of the Northern Ostrobothnia Schist Belt, the North Karelian Schist Belt and one sample from the Kainuu Schist Belt.

from the Kalevian provinces form a rather heterogenous group (Fig. 22).

The Talvivaara dolomite sample (C-266) is so highly depleted in ^{13}C, that it probably does not represent a primary precipitate. Since it is interbedded with graphitic schists, it is therefore conceivable that biogenic carbon has been incorporated in the dolomite. The majority of carbonate samples show $\delta^{13}C_{Tot}$ values between -3.6 and 2.0‰. This range includes also the samples from the Outokumpu Assemblage showing a mean $\delta^{13}C_{Tot}$ value of -2.2±1.0‰.

Two dolomite formations, one at Pitkäselkä, Muhos and another at Varmonniemi, Kesälahti, show ^{13}C-enriched carbon isotope signatures, the $\delta^{13}C_{Tot}$ values being 8.1 and 6.4‰ for the Pitkäselkä and Varmonniemi samples, respectively (Table 5). In this respect they differ from other carbonates from the Kalevian provinces and from all studied sedimentary carbonate formations in the Svecofennian Domain, but are similar to sedimentary carbonates from Jatulian and Ludian formations. This similarity is also reflected lithologically, since like the Jatulian and Ludian, they occur in association with quartzites and graphitic schists.

Age constraints

Ostrobothnia. According to radiometric determinations on zircon the Koiteli Quartzite Formation in the middle of the schist belt was deposited between 2093±35 and 1873±4 Ma (Honkamo, 1988). None of the sedimentary carbonate samples are directly associated with the Koiteli Formation, and, therefore, this time period does not necessarily constrain their sedimentation. Nevertheless, in stratigraphic correlation diagrams presented by Honkamo (1989) samples C-80, Kiiminki and C-163, Vepsä lie roughly at the same stratigraphic level with the Koiteli Formation.

The sedimentary carbonate sample C-164 from Käkiperä resembles the previously mentioned samples both mineralogically and texturally, and it may therefore be related to them. However, these schists may possibly be Archean, as has been suggested by Honkamo (1989) and Kähkönen et al., (1986).

North Karelia. Samples C-120-A, C-120-B, C-231-A and C-231-B from Outokumpu represent the chemical sediments of the Outokumpu Assemblage. A gabbro body amongst serpentinites of the Outokumpu Assemblage has given a zircon age of 1972±18 Ma (Huhma, 1986; Koistinen, 1981). In the absence of any other constraints, it is here assumed that this date corresponds to the depositional age of the whole Outokumpu Assemblage.

Kainuu Schist Belt

Geologic setting

The Kainuu Schist Belt in northeastern Finland (Fig. 1) is one of the major Paleoproterozoic schist belts containing Karelian formations. The belt is bordered on both eastern and western margins by Archean basement of the Karelian craton. The sampling area for this work was in the central part of the schist belt, on the northern side of Lake Oulujärvi (Fig. 23).

The complex geology and stratigraphy of the

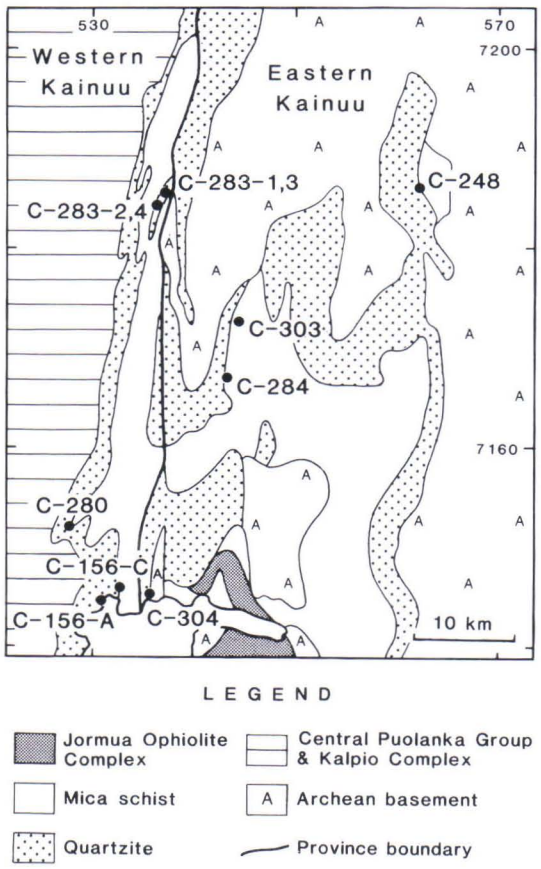

Fig.23. Geological sketch map of the Kainuu Schist Belt based mainly on information in Laajoki (1991), and locations of samples analysed in this study. Also shown is the tectonic line separating the Eastern and Western Kainuu zones.

eastern part of the schist belt in the Puolanka area has been extensively studied by Laajoki and co-workers, and the results have been reviewed recently by Laajoki (1991). The Melalahti area close to the shore of Lake Oulujärvi has been studied by Kärki (1988), while the stratigraphy of the supracrustal rocks in the western Hyrynsalmi area has been described by Kontinen (1986).

A major tectonic line divides the Kainuu Schist Belt into two parts (Fig. 23), which have been called the Eastern and Western Karelides by Laajoki (1991). Here more local names, the Eastern and Western Kainuu zones will be used. The Eastern Kainuu formations are autochthonous to para-autochthonous, but the Western Kainuu formations comprise allochthonous nappe complexes and thrust sheets. Based on lithologic differences and on the existence of an ophiolite complex in the contact area Laajoki (1991) suggested that the Western Kainuu terrain is exotic with respect to the Eastern Kainuu terrain.

Eastern Kainuu. In the study area the lowermost units of the Eastern Kainuu successions are siliciclastic Jatulian type metasediments, which in many places are underlain by a palaeoweathering crust (Kontinen, 1986). In the Hyrynsalmi area these formations are included in the Hyrynsalmi Group, which correlates with the East Puolanka Group in the Puolanka area (Laajoki, 1991). The Hyrynsalmi Group is unconformably overlain by Kalevian metapelites and metaturbidites of the Ristijärvi Group.

Three dolomite samples from the Eastern Kainuu formations have been collected from the Poikkijärvi Formation, which is within the uppermost unit of the Hyrynsalmi Group. One dolomite sample represents a carbonate clast from a turbiditic conglomerate within the Väisälä Formation of the Ristijärvi Group, in which the clasts are interpreted as having been derived largely from the Hyrynsalmi Group (Kontinen, 1986).

Western Kainuu. According to Laajoki (1991) the depositional basement for the allochthonous Western Kainuu successions is unknown, and the formations are present as tectonic slices separated by thrusts. The westernmost units in Figure 23 are the Central Puolanka Group, which is cut by 2.2 Ga metadiabases, but is possibly much older, and the Kalpio Complex, which may represent a metamorphic derivative of the Western Kainuu formations. To the east follow formations of the Vihajärvi and Somerjärvi groups, the latter containing sedimentary carbonate units. The Somerjärvi Group can be traced southwards to

Table 6. Carbon and oxygen isotope data for samples from the Kainuu Schist Belt.

Sample	Location	Dol[1]	$\delta^{13}C$, PDB[2]			$\delta^{18}O$, SMOW[2]	
		wt. %	Tot	Cal	Dol	Cal	Dol
Western Kainuu							
Horkankallio Formation							
C-156-A	Melalahti, Paltamo	40	4.17	3.82	4.38	16.91	18.97
C-156-C	Melalahti, Paltamo	66	3.76	3.30	3.97	21.01	21.41
Salmijärvi Formation, Somerjärvi Group							
C-283-1	Pääkkö, Puolanka	100			3.62		19.76
C-283-3	Pääkkö, Puolanka	86	3.41	2.56	3.70	20.80	20.40
Eskosenvaara Formation, Somerjärvi Group							
C-280	Vuorimäki, Paltamo	99			5.99		20.72
C-283-2	Pääkkö, Puolanka	100			4.21		16.50
C-283-4	Pääkkö, Puolanka	99			4.23		18.30
Eastern Kainuu							
Väisälä Formation, Ristijärvi Group							
C-248	Väisälä, Hyrynsalmi	100			7.54		17.94
Poikkijärvi Formation, Hyrynsalmi Group							
C-284	Kalkkiniemi, Ristijärvi	100			8.20		18.32
C-303	Iso Särkijärvi, Puolanka	80	7.99	7.69	8.17	18.16	15.23
C-304	Koikeronlahti, Paltamo	96	9.10		9.18		16.39

1) Weight-% dolomite in total carbonate by XRD,
2) Tot = Total carbonate, Dol = Dolomite, Cal = Calcite.

the Melalahti area studied by Kärki (1988), where it corresponds to the Melalahti Group. The Somerjärvi Group comprises the Eskosenvaara and Salmijärvi formations and, in addition, the upper part of the Somerjärvi Group contains several poorly exposed tuffitic units.

The Eskosenvaara Formation consists mainly of quartzites, but in the upper part it also contains graphitic and dolomitic intercalations. It is succeeded by the dolomitic Salmijärvi Formation, with the contact between the two formations being a gradual transition. Dolomites of the Salmijärvi Formation are interbedded with graphitic schists and mica schists, and appear to be lithologically correlative with the Ludian group rather than with the Jatulian group of the Kiihtelysvaara–Onega region. The Salmijärvi Formation is overlain by phyllites, iron formations and metaturbidites of the Väyrylä Group (Laajoki, 1991).

The samples from the Western Kainuu formations have been collected from two stratigraphic levels. The lower of these is represented by the Eskosenvaara Formation of the Somerjärvi Group at Puolanka and Paltamo, while the upper level samples were taken from the Horkankallio Formation of the Melalahti Group at Paltamo and the Salmijärvi Formation of the Somerjärvi Group at Puolanka.

$\delta^{13}C$ results

The dolomite contents in the total carbonate fraction and the results of the isotopic analyses

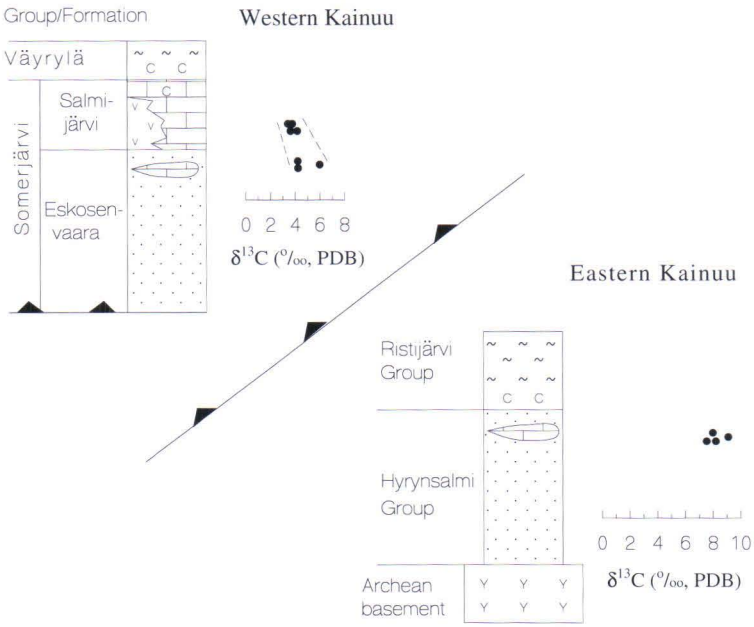

Fig. 24. Partial lithostratigraphic columns for the Eastern and Western Kainuu zones and $\delta^{13}C_{Tot}$ compositions of sedimentary carbonates from the Somerjärvi and Hyrynsalmi groups. Stratigraphic nomenclature for the Western Kainuu area is from Laajoki (1991) and for the Eastern Kainuu area from Kontinen (1986). Symbols as in Fig. 12.

from the Kainuu Schist Belt are given in Table 6 and illustrated together with the stratigraphic columns in Figure 24. Mineralogically the sedimentary carbonate samples are either pure dolomites or mixed calcite-dolomite rocks. The lowest dolomite contents of 40–66% were recorded from the Horkankallio Formation at Melalahti.

Eastern Kainuu. The four dolomite samples from the formations of the Eastern Kainuu schist belt have relatively high $\delta^{13}C_{Tot}$ values, ranging from 7.5 to 9.1‰, with a mean value of 8.2±0.7‰.

Western Kainuu. The sedimentary carbonates from the Eskosenvaara Formation of the Somerjärvi Group show $\delta^{13}C_{Tot}$ values spanning from 4.2 to 6.0‰, with a mean value of 4.8±1.0‰. The $\delta^{13}C_{Tot}$ values of carbonate sampled from the Salmijärvi and Horkankallio formations show a relatively small range from 3.4 to 4.2‰, and the mean value is 3.8±0.2‰.

There is a significant difference in the $\delta^{13}C_{Tot}$ values of carbonate between the formations of the Eastern and Western Kainuu Schist belt. The samples from the Eastern Kainuu are more enriched in ^{13}C relative to the Western Kainuu. In addition, the Western Kainuu formations show some tendency for a decreasing trend in the $\delta^{13}C$ values (Fig. 24).

Age constraints

There are no published age data, from which the depositional age of the sedimentary carbonate formations in the Eastern and Western Kainuu zones could be inferred with reasonable accuracy.

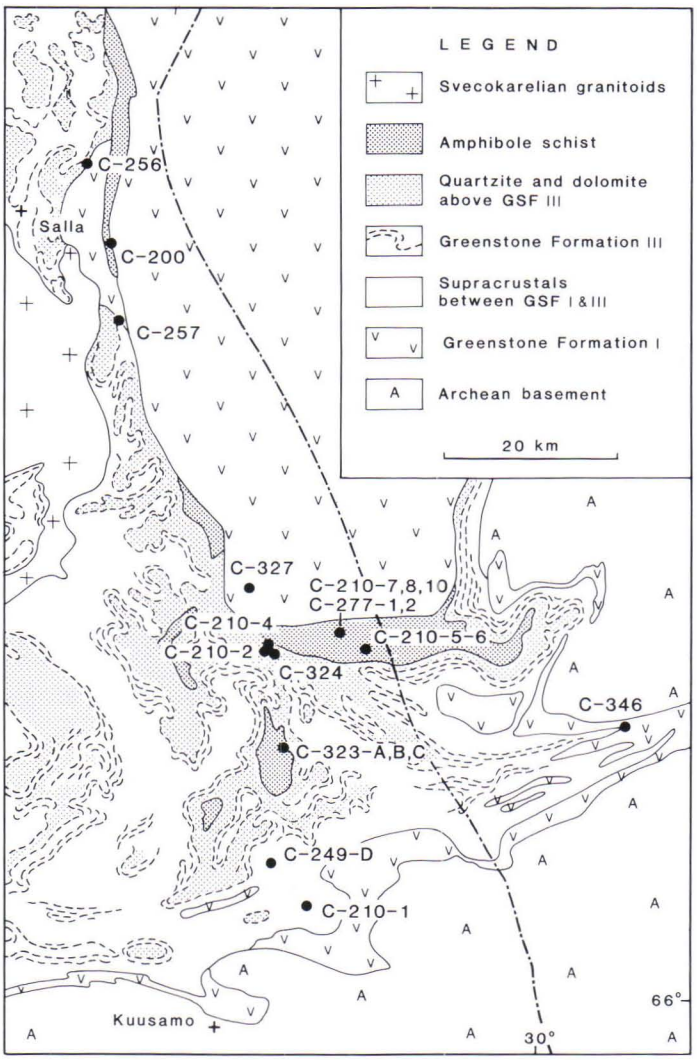

Fig. 25. Geological sketch map of the Kuusamo-Salla schist belt modified mainly from Silvennoinen et al. (1992), Manninen (1991) and Pekkala (1985). Also shown are the sedimentary carbonate sample locations (GSF = Greenstone Formation).

Kuusamo-Salla Schist Belt

The Paleoproterozoic Kuusamo-Salla Schist Belt lies on both sides of the Arctic Circle and straddles the boundary between Finland and Russia (Fig. 1). Geologically it is situated at the junction between several major crustal structures (Silvennoinen, 1992). In the south it is bounded by the Karelian Province, in the east by the Belomorian Province and in the west by the Central Lapland Granite Complex (Fig. 25).

The geology and stratigraphy of the Karelian succession in the Kuusamo area has been studied by Silvennoinen (1972, 1991, 1992). Pekkala (1985) investigated the petrography and geochemistry of the sedimentary carbonate

rocks of the Kuusamo Schist Belt. Recently Manninen (1991) reported on the geology and stratigraphy of the Salla area, which is a direct continuation of the Kuusamo Schist Belt to the north. The geology of the schist belt on the Russian side of the border, in the Paanajärvi-Kuolajärvi area has been reviewed by Kulikov et al. (1980) and Sokolov (1980).

Geologic setting

Kuusamo. The Kuusamo Schist Belt consists of a sedimentary sequence, which appears to have been deposited over a time interval of several hundred millions years, and sedimentary carbonates are present at several stratigraphic levels. Following the lithostratigraphic nomenclature of Silvennoinen (1972) the supracrustal sequence of the Kuusamo Schist Belt begins locally with basal conglomerates, and these are immediately overlain by the intermediate and acid lavas of Greenstone Formation I.

Greenstone Formation I is followed by a transgressive sequence of quartzitic units, which are characterized by herringbone cross-bedding and other tidal features (Silvennoinen, 1992), suggestive of a marine incursion. The sequence commences with the Sericite Quartzite Formation, which is followed by the Sericite Schist and the Quartzite Schist formations. The Sericite Schist Formation includes dolomitic members, some of which have been reported to contain stromatolitic structures (Pekkala, 1985).

The transgression ended with the extrusion of submarine lavas of Greenstone Formation II, and these in turn were followed by the regressive metasedimentary Siltstone Formation. After that vast areas were covered by 200–400 m thick plateau basalts of Greenstone Formation III (Silvennoinen, 1991, 1992).

The plateau basalts are overlain by the Rukatunturi Quartzite Formation and the Dolomite Formation, which in turn is followed by an abrupt change to graphitic schists and tuffites of the Amphibole Schist Formation. Using the terminology of Sokolov (1980), this sharp facies change marks the boundary between the Jatulian and Ludian formations.

Pekkala (1985) recognized the presence of a distinct sedimentary carbonate formation overlying the Amphibole Schist Formation, known as the Limestone-Dolomite Formation, characterized by the presence of both dolomitic and calcitic members. This contrasts with other sedimentary carbonate units in lower stratigraphic positions, in which calcite is rare. This feature is also evident in the dolomite/calcite determinations of Table 7.

In this study the isotopic composition of carbon and oxygen were analysed of 17 sedimentary carbonate samples from four stratigraphic levels of the Kuusamo Schist Belt. Eight of the samples represent the same powders whose geochemistry was studied by Pekkala (1985).

Salla. The continental plateau basalts of Greenstone Formation III can be followed on magnetic maps from Kuusamo northwards to the Salla area, where they are designated as the Tahkoselkä Formation (Manninen, 1991). This formation continues even further northwards into Lapland and therefore it is clearly a key horizon for stratigraphic correlation in northeastern Finland.

Three sedimentary carbonate samples from the Salla area have been analysed in this study. One sample represents the Kelloselkä Formation, comprising the dolomites, arkose quartzites and siltstones occurring below the basalts of the Tahkoselkä Formation. Another has been collected from the dolomitic portion of the Matovaara Formation lying stratigraphically above the Tahkoselkä Formation. The Matovaara Formation consists largely of orthoquartzites and siltstones (Manninen, 1991) and corresponds to the Rukatunturi Formation in the Kuusamo area. The third sample is from dolomites associated with graphitic schists of the Aatsinginhauta Formation.

Table 7. Carbon and oxygen isotope data for samples from the Kuusamo and Salla schist belts.

Sample	Location	Dol[1]	$\delta^{13}C$, ‰, PDB[2]			$\delta^{18}O$, ‰, SMOW[2]	
		wt. %	Tot	Cal	Dol	Cal	Dol
Kuusamo Schist Belt							
Limestone-Dolomite Formation							
C-210-5	Liikasenvaara, Kuusamo	98	5.82		5.90		20.94
C-210-6	Liikasenvaara, Kuusamo	17	3.29	3.22	3.88	21.33	21.65
C-210-7	Autiolampi, Kuusamo	98	2.59		2.72		18.47
C-210-8	Autiolampi, Kuusamo	100			3.70		21.15
C-210-10	Autiolampi, Kuusamo	22	3.38	3.31	4.17	17.32	18.58
C-277-1	Autiolampi, Kuusamo	100			3.74		21.57
C-277-2	Autiolampi, Kuusamo	100			3.77		20.71
Dolomite Formation							
C-210-2	Kiutaköngäs, Kuusamo	100			10.41		18.13
C-210-4	Puukkorinne, Kuusamo	1	15.03	15.07		20.45	
C-323-A	Kuopunki, Kuusamo	100			8.17		20.36
C-323-B	Kuopunki, Kuusamo	100			11.20		22.14
C-323-C	Kuopunki, Kuusamo	100			10.98		19.36
C-324	Kiutaköngäs, Kuusamo	100			8.21		17.20
C-327	Asentolampi, Kuusamo	98	10.54		10.61		18.55
Siltstone Formation							
C-210-1	Vaimojärvi, Kuusamo	100			12.10		14.30
Sericite Schist Formation							
C-249-D	Särkilampi, Kuusamo	100			8.18		13.51
C-346	Paanajärvi, Russia	92	8.10		8.21		14.85
Salla Schist Belt							
Aatsinginhauta Formation							
C-200	Könkäänmaa, Salla	100			7.10		20.89
Matovaara Formation							
C-256	Sompsuripalo, Salla	100			9.88		20.49
Kelloselkä Formation							
C-257	Hanhioja, Salla	0	12.70	12.71		17.71	

1) Weight-% dolomite in total carbonate by XRD,
2) Tot = Total carbonate, Dol = Dolomite, Cal = Calcite.

$\delta^{13}C$ results

Dolomite contents in the total carbonate fraction and the carbon and oxygen isotope analyses from the Kuusamo and Salla areas are listed in Table 7. The $\delta^{13}C_{Tot}$ values are illustrated with respect to the stratigraphic column in Figure 26. The datapoints from the Salla area are given as open circles to distinguish them from the Kuusamo samples.

Apart from the uppermost Limestone-Dolomite Formation all sedimentary formations

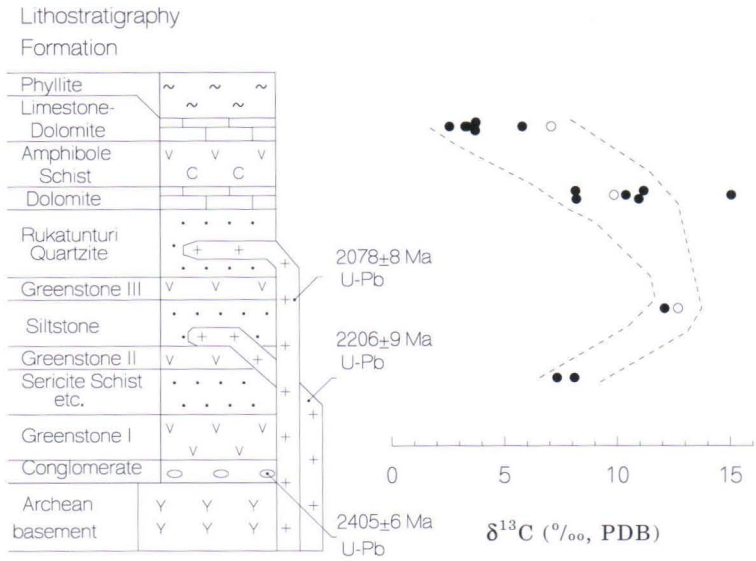

Fig. 26. Lithostratigraphy of the Kuusamo Schist Belt modified from Silvennoinen (1972, 1991) and Pekkala (1985), also showing the variation in $\delta^{13}C_{Tot}$ compositions of sedimentary carbonates throughout the stratigraphic column. Samples from the Salla Schist Belt have been included in inferred correlative formations, based on the extrapolation of Greenstone Formation III and the Amphibole Schist Formation to the Salla area. Symbols as in Fig. 12.

studied show unusually high $\delta^{13}C_{Tot}$ values varying from 8.1 to 15.0‰, which are considerably higher than those reported by Veizer et al. (1992a,b) for Paleoproterozoic carbonates.

The $\delta^{13}C_{Tot}$ values of the sedimentary carbonates define a trend that first increases from 8.1±0.1‰ in the Sericite Schist Formation to 12.4±0.4‰ in the Siltstone Formation, and then decreases to 10.6±2.1‰ in the Dolomite Formation and finally to 4.2±1.5‰ in the Limestone-Dolomite Formation. In calculating the averages, the Salla samples were included in their inferred correlative formations; their removal from the dataset would not significantly affect the results.

Age constraints

The supracrustal sequence in the Kuusamo area is cut by albite diabase dikes and sills of different generations. U-Pb ages from diabases at Jäkäläniemi and at Viipus (Silvennoinen, 1991) set important constraints on the timing of sedimentation in the Kuusamo Schist Belt.

The diabase sill at Jäkäläniemi is dated at 2206±9 Ma, which is based on zircons, on two concordant titanite fractions and on a nearly concordant baddeleyite fraction. The Viipus diabase sill has yielded an age of 2078±8 Ma, which has been calculated from two transparent, discordant zircon fractions and three titanite fractions, two of which are nearly concordant. A maximum age for the supracrustal succession of the Kuusamo area is provided by a zircon dating of 2405±6 Ma from three quartz-porphyry pebbles from the basal conglomerate (Silvennoinen, 1991).

The Jäkäläniemi diabase has been observed to cut both Greenstone Formation II and Siltstone Formation. The younger Viipus diabase cuts the lower part of the Rukatunturi Quartzite Formation. No albite diabases have been found to cut the Amphibole Schist Formation, which led Silvennoinen (1991) to suggest that the younger diabase generation possibly represented feeder conduits for the Amphibole Schist

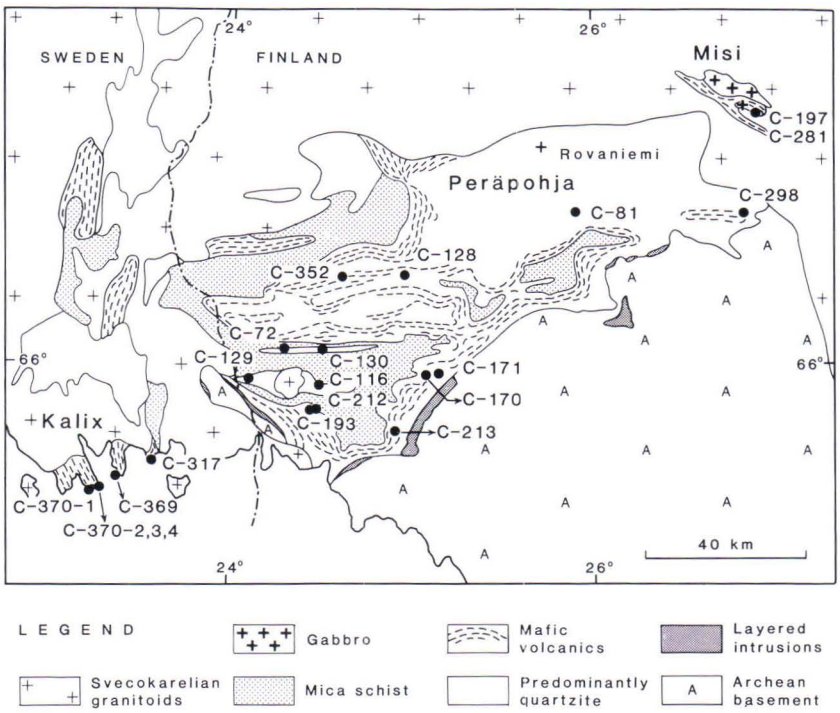

Fig. 27. Geological sketch map showing the Peräpohja and Misi schist belts and the Kalix Greenstone Belt and the locations of samples collected from these areas. The map has been modified from Geological Map, Northern Fennoscandia (1987), Perttunen (1989) and Ödman (1957).

Formation.

The age of the Jäkäläniemi diabase sill demonstrates, that the lowermost ^{13}C-enriched carbonates from the Kuusamo district were deposited before 2206 Ma, but after 2405 Ma. The large drop in $\delta^{13}C_{Tot}$ values from 10.6‰ in the Dolomite Formation down to 4.2‰ in the Limestone-Dolomite Formation is roughly contemporaneous with the deposition of the Amphibole Schist Formation (see Fig. 26), possibly at about 2070 Ma ago.

Peräpohja Schist Belt and Misi area

The Peräpohja Schist Belt in northern Finland (Fig. 1) covers an east-west trending area of about 130x50 km^2 bounded to the north by the Central Lapland Granite Complex and to the south by the Archean Basement Complex (Fig. 27). The Misi area is an isolated schist belt totally enclosed in the Central Lapland Granite Complex close to the eastern extremity of the Peräpohja Schist Belt (Fig. 27).

Geologic setting

Peräpohja. The geology and lithostratigraphy of the Peräpohja Schist Belt has been described by Perttunen (1985, 1989, 1991), and general geologic features are shown in Figure 27. The succession overlies the Archean Basement Complex and the 2.44 Ga layered intrusions, and locally there is a weathering

crust present between the lowermost formations and the basement. This paleoregolith marks the lower boundary of the Jatulian formations in this area.

The weathering crust is followed by the siliciclastic Sompujärvi Formation, which also locally includes dolomitic interlayers. The Sompujärvi metasediments are followed by the subaerial lava flows of the Runkaus Formation, which is overlain by the fluvial metasediments of the transgressive Kivalo Formation. The Kivalo Formation is composed largely of quartzites, but in the uppermost units pink dolomite is also present.

The Kivalo Formation is followed by the subaerial lavaflows of the Jouttiaapa Formation and the tidal orthoquartzites of the Kvartsimaa Formation, which display oscillating crossbedding, ripple marks, mudcracks and occasional dolomite interlayers.

The Kvartsimaa Formation is overlain by the mafic tuffites of the Tikanmaa Formation and the 100 to 300 m thick Rantamaa Dolomite Formation. Dolomites in both the Kvartsimaa and the Rantamaa formations show distinct stromatolitic structures, which have been described by Härme & Perttunen (1964) and Krylov & Perttunen (1978).

Misi. The geology of the Misi area has been described by Nuutilainen (1968). Although that work concentrates largely on the geology and genesis of the iron ores in the Misi area, stratigraphic relations of the supracrustal succession are also described.

Most of the Misi area is composed of gabbro and apparently volcanogenic amphibolite. In addition, there are more local zones or lenses of metasedimentary sequences including quatzites, mica schists, graphitic schists and dolomite rocks. These are often completely enclosed by gabbro and associated albite rocks.

There appears to be no doubt that the metasedimentary units are older than the enclosing gabbro (Nuutilainen, 1968). The stratigraphic succession of the metasediments is more difficult to ascertain, as primary structures generally have not been preserved. However, Nuutilainen (1968) suggested that the metasedimentary succession starts with quartzites, which are followed by mica schists and dolomite rocks.

The dolomite samples from the Misi area were all collected from material derived from the Raajärvi iron ore prospect.

$\delta^{13}C$ results

Analytical results for the Peräpohja Schist Belt and for the Misi area are listed in Table 8. The $\delta^{13}C_{Tot}$ values of carbonate are illustrated together with the stratigraphic column in Figure 28 for the Peräpohja samples and in Figure 29 for the Misi samples.

Peräpohja. The general systematics of the evolution of the $\delta^{13}C_{Tot}$ values of carbonate in the Peräpohja samples resembles the stratigraphic variation in the Kuusamo area. With the exception of the uppermost Rantamaa Formation, carbonate in the samples from all other formations is enriched in ^{13}C relative to normal sedimentary material (Fig. 28).

A dolomite sample from the lowermost Sompujärvi Formation yielded a $\delta^{13}C_{Tot}$ value of 8.6‰. Dolomites in the upper part of the Kivalo Formation have a similar mean $\delta^{13}C_{Tot}$ value of 7.9±1.9‰, and the analysed samples from the Kvartsimaa Formation also show analogous high $\delta^{13}C$ values, with a mean $\delta^{13}C_{Tot}$ value of 8.6±0.5‰. There appears to be no significant differences in the carbon isotope compositions of carbonate between these formations.

However, the systematics of the $^{13}C/^{12}C$ ratios of carbonate in the Rantamaa Formation is different. The $\delta^{13}C_{Tot}$ values of carbonate samples range from highly enriched compositions of 11.4 down to 2.5‰. In addition, there appears to be some regularity in the distribution of these values within the formation, as is described below.

The Miihkailinmaa (C-170) drill hole intersected the contact between the Tikanmaa and the Rantamaa formations, and it apparently includes samples from the lowest level in the

Table 8. Carbon and oxygen isotope data for samples from the Peräpohja and Misi schist belts.

Sample	Location	Dol[1]	$\delta^{13}C$, ‰, PDB[2]			$\delta^{18}O$, ‰, SMOW[2]	
		wt. %	Tot	Cal	Dol	Cal	Dol
Peräpohja Schist Belt							
Rantamaa Formation							
C-72	Korkeamaa, Tornio	100			2.91		22.84
C-116	Rantamaa, Tornio	100			5.16		21.96
C-128-1	Louepalo, quarry 1, Tervola	100			2.50		21.66
C-128-2	Louepalo, quarry 2, Tervola	100			3.63		23.80
C-128-3	Louepalo, Tervola	100			4.14		23.16
C-129	Kukkola, Tornio	82	7.1	6.86	7.19	19.59	18.46
C-130	Korpijärvi, Tornio	100			5.44		19.70
C-212-A	Kalkkimaa, Tornio	98			7.41		20.66
C-212-B	Kalkkimaa, Tornio	100			8.49		19.45
C-170-A	Miihkailinmaa, Tervola	100			11.13		21.44
C-170-B	Miihkailinmaa, Tervola	99			11.44		21.26
C-170-C	Miihkailinmaa, Tervola	100			11.29		20.67
C-170-D	Miihkailinmaa, Tervola	100			9.63		20.74
Kvartsimaa Formation							
C-193-A	Kvartsimaa, Tornio	100			8.31		14.03
C-193-B	Kvartsimaa, Tornio	100			9.21		19.86
C-193-C	Kvartsimaa, Tornio	100			8.42		16.27
Kivalo Formation							
C-81	Taipale, Rovaniemi mlk.	98	8.33		8.45		17.46
C-171-A	Palokivalo, Tervola	100			10.55		18.02
C-171-C	Palokivalo, Tervola	100			7.10		20.13
C-171-D	Palokivalo, Tervola	100			6.93		20.19
C-171-E	Palokivalo, Tervola	100			5.22		23.20
C-213	Kalliokoski, Keminmaa	100			9.53		17.50
C-298-A	Kalkkinulkki, Rovaniemen mlk	100			10.01		13.10
Sompujärvi Formation							
C-352-A	Santalampi, Tervola	100			8.56		14.84
Misi area							
C-197	Raajärvi, Kemijärvi	82	12.78	12.33	12.94	20.47	19.63
C-281-1	Raajärvi, Kemijärvi	94	12.20		12.35		20.28
C-281-2	Raajärvi, Kemijärvi	100			12.81		21.15
C-281-3	Raajärvi, Kemijärvi	77	12.11	11.61	12.36	17.66	20.21
C-281-4	Raajärvi, Kemijärvi	88	12.90		13.01		19.21

1) Weight-% dolomite in total carbonate by XRD,
2) Tot = Total carbonate, Dol = Dolomite, Cal = Calcite.

Rantamaa Formation, from only 4 to 11 m above the contact surface (Appendix 1). At present it is not possible to arrange the Rantamaa samples in stratigraphic order, and, therefore, only two distinct groups will be considered. The samples from the Miihkailinmaa

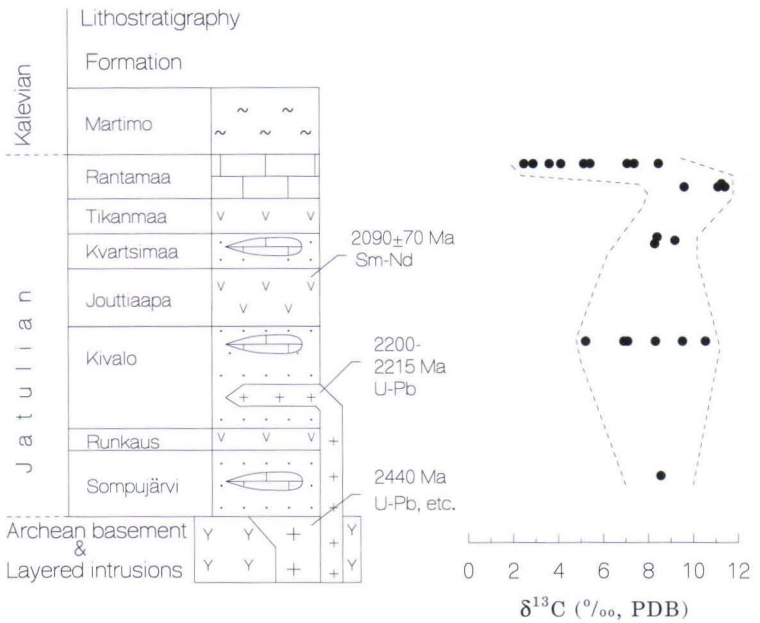

Fig. 28. Lithostratigraphy of the Peräpohja Schist Belt based on information in Perttunen (1985, 1991) and Huhma et al. (1990), also showing the variation in $\delta^{13}C_{Tot}$ compositions of sedimentary carbonates through the stratigraphic column. Symbols as in Fig. 12.

drill core are considered as representing the lower Rantamaa Formation, and all other samples are thought to represent the upper Rantamaa Formation.

The mean $\delta^{13}C_{Tot}$ value for the lower Rantamaa samples is 10.7±0.8‰, which means, that dolomites of the lower Rantamaa Formation are the most enriched in ^{13}C yet found within the Peräpohja Schist Belt. In contrast, the upper Rantamaa Formation records a mean $\delta^{13}C_{Tot}$ value of 5.2±2.1‰, which is lower than the corresponding mean values for other formations. Thus, the Rantamaa Formation apparently records a transition from dolomites highly enriched in ^{13}C in the lower part of the section to dolomites only moderately enriched in ^{13}C in the upper part of the section.

Misi. The carbon isotope compositions of carbonate from the Raajärvi mine in the Misi area are tightly clustered, showing a mean $\delta^{13}C_{Tot}$ value of 12.6±0.4‰ (Fig. 29). Of all the sedimentary formations in this study, the Misi dolomite unit is the most enriched in ^{13}C. Although the carbon isotope compositions are exceptional, the $\delta^{18}O$ values of dolomite are similar to those of other carbonate units, ranging from 19.2 to 21.2‰ (Table 8).

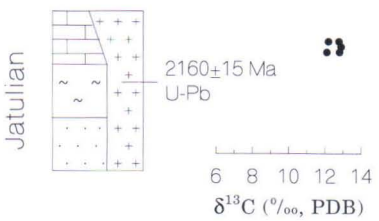

Fig. 29. Schematic stratigraphic column of the Misi schist belt presented according to the interpretation of Nuutilainen (1968) and the radiometric results of Patchett et al. (1981). Also shown are the $\delta^{13}C_{Tot}$ compositions of sedimentary carbonates. Symbols as in Fig. 12.

Age constraints

Peräpohja. Radiometric age data for layered intrusions, mafic metavolcanics and albite diabases in the Peräpohja area have been reported by Alapieti (1982), Huhma et al. (1990) and Perttunen (1991); some of these results are shown schematically in Figure 28.

Layered intrusions at the base of the supracrustal sequence have been dated by U-Pb, Pb-Pb and Sm-Nd-methods, and all results point to an intrusion age of about 2440 Ma (Alapieti, 1982; Huhma et al., 1990). Zircon, titanite and baddeleyite from the albite diabase sills within the quartzites of the Kivalo Formation have yielded ages from 2121 to 2215 Ma (Perttunen, 1991). These results imply that the dolomite beds of the Sompujärvi Formation were deposited before 2210 Ma (see Fig. 28).

The mafic metalavas of the Jouttiaapa Formation have been dated as 2090±70 Ma (Huhma et al., 1990). The Jouttiaapa Formation is underlain by the dolomite beds of the Kivalo Formation and is overlain by the quartzites and dolomite intercalations of the Kvartsimaa Formation; both these formations contain carbonate enriched in ^{13}C, with an average $\delta^{13}C_{Tot}$ value of 7.9‰ in the former and 8.6‰ in the latter.

The Rantamaa dolomite Formation, which seems to be characterized by a large drop in the $\delta^{13}C_{Tot}$ values, was deposited after 2090±70 Ma.

Misi. The large gabbro body in the Misi area has yielded a U-Pb zircon age of 2160±15 Ma (Patchett et al., 1981). Based on the geologic evidence the gabbro intrusion is younger than the sedimentary units of the Misi area (Nuutilainen, 1968). Therefore, in the Misi area the deposition of the highly ^{13}C enriched carbonate units is constrained to have occurred before that time.

Kalix Greenstone Belt

The Kalix Greenstone Belt lies at the northern end of the Gulf of Bothnia in Sweden, about 40 km west of the southwestern margin of the Peräpohja Schist Belt (Fig.27). The Kalix and the Peräpohja supracrustal belts are separated by synorogenic granitoid intrusions, and possibly also by one arm of a large north-south trending tectonic zone described by Berthelsen & Marker (1986b).

Geologic setting

Although the distance between the Kalix and Peräpohja supracrustal belts is small, their stratigraphic successions are not readily correlated. As the names indicate, the Kalix Greenstone Belt is dominated by metavolcanic rocks and the Peräpohja Schist Belt by metasedimentary rocks. One notable difference in this respect is the absence of thick Kivalo type quarzites in the Kalix area, where the quartzite units reach a thickness of only a few tens of meters (Lager & Loberg, 1990). This is much less than the thickness of the Kivalo Formation in the Peräpohja Schist Belt, where it varies from 1000 to 2000 m (Perttunen, 1991).

The sedimentology and lithostratigraphy of the Kalix Greenstone Belt has been investigated by Lager & Loberg (1990). A summary of the lithostratigraphic relations has also been presented by Öhlander et al. (1992), who attempted to determine the age of the Kalix succession using the Pb-Pb method on carbonate rocks.

The supracrustal sequence of the Kalix area has been divided into three groups referred to as the Lower, Middle and Upper groups (Lager & Loberg, 1990). The depositional basement is unknown. The Lower Group consists predominantly of terrestrial, mafic metalavas, which are separated from the Middle Group by an unconformity and a weathering crust.

The Middle Group comprises three formations, respectively the Lower, the Middle and

Table 9. Carbon and oxygen isotope data for samples from the Kalix Greenstone Belt in Sweden.

Sample	Location	Dol[1]	$\delta^{13}C$, ‰, PDB[2]			$\delta^{18}O$, ‰, SMOW[2]	
		wt. %	Tot	Cal	Dol	Cal	Dol
Upper formation, Middle group							
C-370-1	Lutskäret, Kalix	100			4.77		16.93
C-370-2	Vitgrundet, Kalix	100			4.18		18.96
C-370-3	Vitgrundet, Kalix	100			3.93		17.98
C-370-4	Vitgrundet, Kalix	100			3.45		20.79
Lower formation, Middle group							
C-317-A	Bodölandet, Kalix	93	2.68		2.67		20.64
C-317-B	Bodölandet, Kalix	87	2.59	1.92	2.67	22.63	22.27
C-369	Trutskärsgrund, Kalix	69	3.37	2.66	4.08	18.86	17.36

1) Weight-% dolomite in total carbonate by XRD,
2) Tot = Total carbonate, Dol = Dolomite, Cal = Calcite.

the Upper Formation (Lager & Loberg, 1990). The Lower Formation contains mafic metalavas, volcanoclastics, quartzites and limestones and dolomites. Quartzite beds show bidirectional crossbedding indicating a tidal environment. Dolomites include intertidal stromatolite beds and supratidal calcrete beds. The Middle Formation is largely composed of mafic terrestrial metalavas. The Upper formation is dominated by a dolomite succession containing numerous stromatolite beds.

The Upper Group consists mainly of mica schists with graphitic and carbonate interlayers.

Sedimentary carbonate samples for isotopic analysis were included from the Lower and Upper formations of the Middle Group and therefore represent two different stratigraphic levels.

$\delta^{13}C$ results

The dolomite contents in the total carbonate fraction and the carbon and oxygen isotope ratios of samples from the Kalix Greenstone Belt are given in Table 9, and the $\delta^{13}C_{Tot}$ values of carbonate are also illustrated relative to the schematic stratigraphic column in Figure 30.

The mean $\delta^{13}C_{Tot}$ value of carbonate for samples from the Lower Formation of the Middle Group is 2.9±0.4‰ and for those from the Upper Formation it is 4.1±0.5‰. Sedimentary carbonates from the Kalix Greenstone Belt are not strongly enriched in ^{13}C compared to dolomite rocks from the Peräpohja Schist Belt or from the Misi area. In the Peräpohja area only the upper Rantamaa Formation contains dolomites with similar carbon isotope signatures.

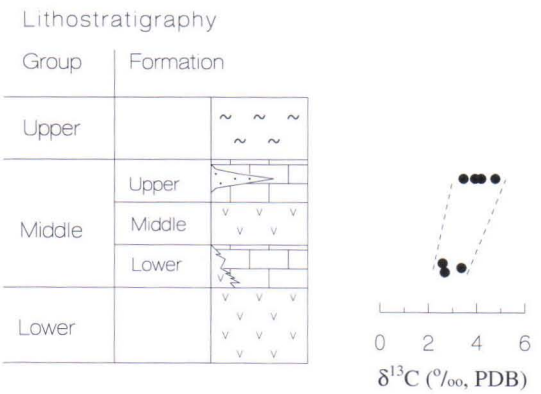

Fig. 30. Lithostratigraphy of the Kalix Greenstone Belt after Lager & Loberg (1990) and Öhlander et al. (1992), also showing the $\delta^{13}C_{Tot}$ compositions of sedimentary carbonates in the Lower and Upper formations of the Middle Group. Symbols as in Fig. 12.

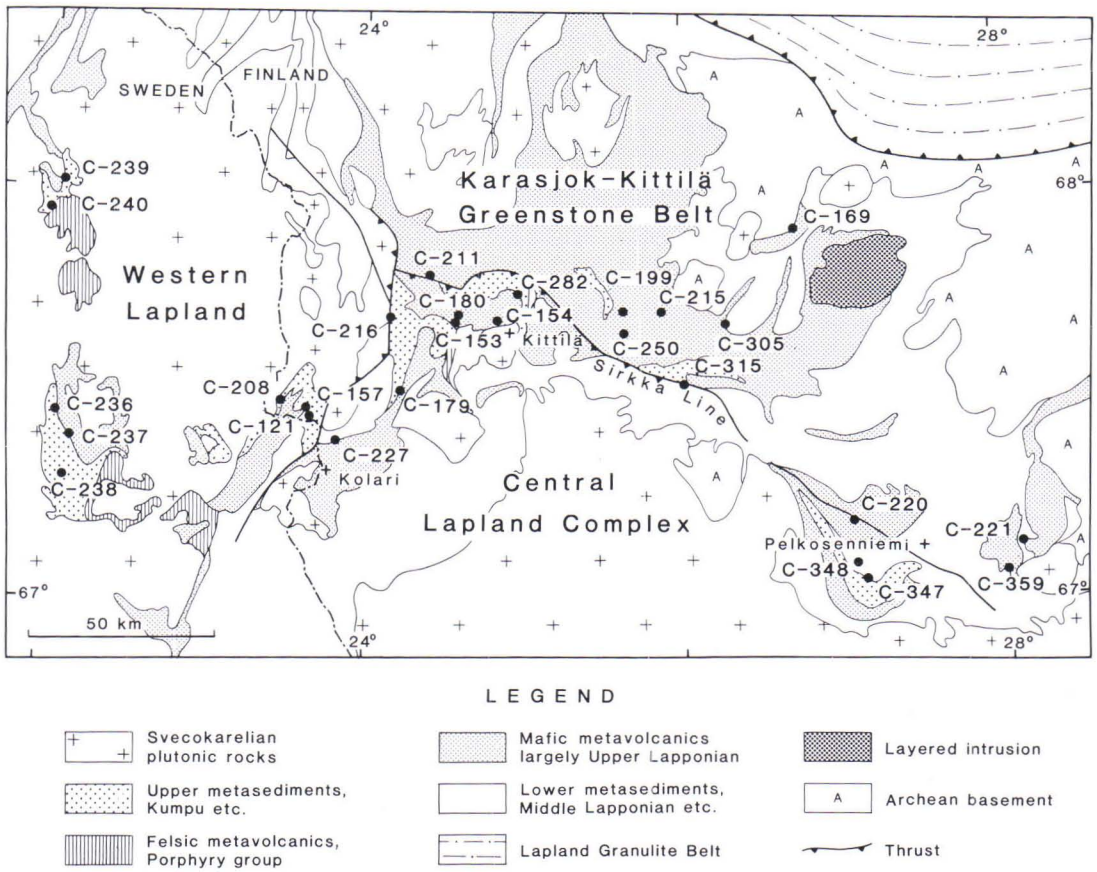

Fig. 31. Geological sketch map of the Central Lapland region largely after Geological Map, Northern Fennoscandia (1987) showing the sample locations. The boundaries between subprovinces are drawn along major tectonic zones (see Gaál et al., 1989; Lehtonen et al., 1992).

Central Lapland region

An extensive Paleoproterozoic supracrustal belt is present on the southwestern side of the Lapland Granulite Belt in central Lapland, extending across the territories of Finland, Sweden and Norway. The belt is bounded to the northwest by allochthonous and autochthonous Caledonian units and to the south is intruded by the Central Lapland Granite Complex (Figs. 1 and 31).

The depositional age of these supracrustal rocks has aroused a great deal of controversy. Based on a few Archean zircon dates and other evidence most of the supracrustal succession had previously been assigned as being latest Archean (Silvennoinen et al., 1980; Gaál et al., 1978). Recently, however, Lehtonen et al. (1992) have accepted the alternative viewpoint, that this rock sequence was deposited on the Archean basement in Paleoproterozoic times.

General geologic setting

Lehtonen et al. (1992) divide the supracrustal formations deposited on the Archean basement in Central Lapland into five groups. Starting from the bottom these are the Lower, Mid-

dle and Upper Lapponian groups, the Lainio Group and the Kumpu Group.

Lower Lapponian formations are present only locally and consist mainly of ultramafic to felsic lavaflows and pyroclastics, although minor sedimentogenic interbeds are also present. The Lower Lapponian Group has been reported as being separated from the metasediments of the Middle Lapponian Group by a weathering crust, although there is no evidence for a regional unconformity. The Middle Lapponian formations include arkosic quartzites, orthoquartzites, mica schists and sedimentary carbonate rocks (Lehtonen et al., 1992).

The Upper Lapponian Group is composed of three metavolcanic units. The lowermost unit consists of high-Mg basaltic and komatiitic lava flows with interbedded pyroclastic deposits. These komatiites are overlain by two tholeiitic units separated by the Porkonen Iron Formation.

The metavolcanic formations of the Upper Lapponian Group are followed by the largely metasedimentary Lainio and Kumpu groups. Originally Mikkola (1941) included both these groups in the Kumpu formation, However, it was later shown that some of these formations predate and some postdate the Svecokarelian orogenic deformation, and accordingly, this feature is now considered to form the boundary between the Lainio and Kumpu groups (Lehtonen, et al., 1992).

The Lainio group comprises polymictic conglomerates, fluvial quartzites and siltstones. Also included in the Lainio Group is the volcanic Latvajärvi Formation, which is formed of porphyritic intermediate and felsic volcanics. The sediments of the Kumpu Group consist mainly of fluvial and shallow water conglomerates and quartzites, which were deposited unconformably on deformed Lapponian volcanics.

Tectonostratigraphic subdivision

The stratigraphic scheme presented above is a simplified generalization portraying complicated patterns of deposition of supracrustal formations in the central Lapland region, and thus the interpretations given above may be inadequate. For instance, if an attempt is made to arrange the $^{13}C/^{12}C$ ratios of sedimentary carbonates according to their positions in the stratigraphic column, the $\delta^{13}C$ values do not show any systematical trends or variations. In contrast, the Middle Lapponian, the Upper Lapponian and even the Lainio Group all contain both ^{13}C-enriched and normal sedimentary carbonates.

A lack of systematics in the $\delta^{13}C$ values is conceivable, but because the variations in $\delta^{13}C$ values in many other Paleoproterozoic supracrustal belts appear to be systematic, this might also be expected to be the case in Lapland. If this were so, the apparently random distribution of the $^{13}C/^{12}C$ ratios would be an artifact of the stratigraphic model. As an attempt to resolve this problem the Central Lapland area is here divided into four tectonostratigraphic subprovinces, which will be treated separately.

Gaál et al. (1989) divided the the Central Lapland area into two subprovinces separated by thrust faults along the Sirkka Line. The northern, largely metavolcanic area is called the Karasjok–Kittilä Greenstone Belt and the southern, dominantly metasedimentary subprovince is called the Central Lapland Complex. The latter will be here further divided into two geographically separate subareas, namely the Kittilä-Kolari area in western Lapland and the Pyhätunturi area at Pelkosenniemi in eastern Lapland (Fig. 31).

To the west the Sirkka Line terminates against a belt of north-south trending shear zones (cf. Lehtonen et al., 1992; Berthelsen & Marker, 1986b; Gaál et al., 1989). The subprovince on the western side of these shear zones, mainly in northern Sweden, is here called the Western Lapland area.

Geologic setting of subareas

Pyhätunturi, Pelkosenniemi. The sedimentology and lithostratigraphy of the conglomer-

ate-orthoquartzite sequence at Pyhätunturi has been investigated by Räsänen & Mäkelä (1988), who considered it to be part of the Kumpu formation. Its stratigraphic position relative to the Lainio Group and Kumpu Group (Lehtonen et al., 1992) nevertheless is uncertain.

According to the description of Räsänen & Mäkelä (1988), the lowermost stratigraphic units in the Pyhätunturi area consist of Lapponian supracrustal rocks, which include mica schists, metavolcanics and quartzites. These are overlain by the coarse clastic, fluvial Isokuru and Pyhätunturi formations, and these in turn by the lava flows of the Kiimaselkä Formation.

Sampling localities are shown in Figure 31. A total of five sedimentary carbonate samples were included in the work from the Pyhätunturi area. Three of these samples have been collected from outcrops, which according to the stratigraphic column of Räsänen & Mäkelä (1988) would be lying above the Pyhätunturi group. However, according to J. Räsänen (personal communication, 1993) the stratigraphy of Räsänen & Mäkelä (1988) is not correct in this respect, and all carbonates in this work seem to lie stratigraphically below the Isokuru and Pyhätunturi formations. This interpretation is presented schematically in Figure 32.

Two of the samples have been collected from the Kalkkivaara area at the River Kitinen and the other two from the Pyhäjoki area 12 km further south. These occurrences do not necessarily represent the same carbonate horizons, but they do, however, share one unusual mineralogic feature. Eskola et al. (1919) reported the existence of brownish albite crystals in the Kalkkivaara dolomites. The Kalkkivaara samples analysed in this study are calcite rocks and do not contain albite, but the sample C-348-B from Pyhäjoki is characterized by brownish, idiomorphic albite crystals.

Kittilä–Kolari. The Archean basement is not exposed in the Kittilä–Kolari area of the Central Lapland Complex, but otherwise the succession appears to be nearly complete including the Lower, Middle and Upper Lapponian groups, the Lainio Group and the Kumpu Group (Fig. 33). However, it is notable that the ultramafic komatiites from the lower part of the Upper Lapponian Group are absent (see Lehtonen et al., 1992).

The samples represent sedimentary carbonate units from among the Middle Lapponian metasediments and the Upper Lapponian volcanics, and, in addition, one sample was obtained from carbonate rock intercalations within the Lainio Group. The Upper Lapponian Group also includes the Rautuvaara Formation in the Kolari area (Hiltunen, 1982; Väänänen, 1989).

The Middle Lapponian dolomite occurrence at Kuoninkivaara (C-315) lies in the immediate vicinity of the Sirkka Line among tidal quartzites (Nikula, 1988). The metasedimentary rocks in this area are intruded by numerous metadiabase bodies, and the area has been subject to large scale hydrothermal alteration (Eilu, 1993).

The $\delta^{18}O$ values of dolomite in the middle Lapponian Kuoninkivaara occurrence range from 11.3 to 12.1‰ (Table 10) and are unusually low, if they represent original depositional conditions. More probably therefore their low $\delta^{18}O$ values are related to large scale hydrothermal alteration and albitization, which has affected the Kuoninkivaara area and its surroundings.

In spite of the evidence for hydrothermal alteration, the dolomite samples from Kuoninkivaara were accepted partly because this dolomite unit is one of the rare examples of carbonate depostion before 2.2 Ga, and partly for the reason that they are without doubt primary metasediments. In addition, petrographical investigations showed no evidence of reactions between dolomite and silicates, and dolomite samples have retained their highly positive $\delta^{13}C$ values.

Karasjok–Kittilä. The following description applies mainly to the southern part of the

Karasjok–Kittilä Greenstone Belt, and follows the lithostratigraphic classification of Lehtonen et al. (1992). The supracrustal sequence on the northern side of the Sirkka Line was deposited discordantly on the Archean basement. The Paleoproterozoic succession starts with the Lower Lapponian Group, which consists largely of volcanic rocks. These are followed by the Middle Lapponian metasediments, which are largely quartzites, but in the upper part of the section mica schists, dolomites and graphitic schists are also found (Lehtonen et al., 1992; Juopperi & Räsänen, 1989).

Deposition of the graphitic schists was followed by a phase of explosive komatiitic magmatism represented by the Sattasvaara Formation, which resulted in a chain of ultramafic pyroclastics extending from Karasjok in Norway at least as far as Salla in northeastern Finland, near the Russian border (Lehtonen et al., 1992; Saverikko, 1987; Pihlaja & Manninen, 1988). In addition, the unit also contains komatiitic lava flows and high-Mg tholeiites. This dominantly ultramafic unit is the lowermost formation of the Upper Lapponian Group.

The Sattasvaara Formation is overlain by two tholeiitic units, the Kautoselkä and Vesmajärvi formations, which are separated from each other by the Porkonen Iron Formation (Lehtonen et al., 1992).

The Lainio Group appears to be absent from the Karasjok–Kittilä Greenstone Belt, but the coarse clastic sediments of the Kumpu Group are present locally and unconformably overlie the Upper Lapponian Group.

This study includes samples from all three Lapponian groups. Sedimentary carbonates are rare in the Lower Lapponian, and a single sample was obtained from the Peurasuvanto area, where the geology has been described by Peltonen et al. (1988) and Pihlaja & Manninen (1988). Several samples represent the dolomite-black shale unit lying in the transition zone between the Middle and Upper Lapponian groups, as shown schematically in Fig. 34. Two of these transition zone samples (C-305-2 & 3, Rajala) have been included in the Sattasvaara Formation, because in the drill core section (Fig. 35) they can be observed to occur stratigraphically above the lowest ultramafic beds. Five sedimentary carbonate samples represent the Kautoselkä Formation, stratigraphically above the Sattasvaara Formation.

Western Lapland. Witschard (1984) suggested a general stratigraphic column for the Paleoproterozoic supracrustal sequence in western Lapland. Starting from the base these units are the Lower Sediment Group, the Greenstone Group, the Middle Sediment Group, the Porphyry Group and the Upper Sediment Group.

In this work samples have been included from only two stratigraphic levels. Most of the samples have been taken from the upper part of the Greenstone Group and one calcitic sample (C-128, Tiankijoki) represents the Middle Sediment Group.

The Greenstone Group includes samples from the upper part of the Veikkavaara Greenstone Group (C-236-A,B, Masugnsbyn; C-237, Hietajoki) and from the upper part of the Kiruna Greenstone Group (C-239, Kivivaara; C-240, Huornaisenvuoma). The geology of the Veikkavaara Greenstone Group and the associated rocks has been described by Padget (1970) and that of the Kiruna Greenstone Group by Ambros (1980). According to Padget (1970), the correlation of these two greenstone groups seems indisputable.

Also included in the same group are samples from the Mannakorpi (C-208) and Äkäsjoki (C-121, C-157) areas in northwestern Finland. These sedimentary units represent continuations of the metasedimentary upper part of the Kaunisvaara Greenstone Group on the Finnish side of the border with Sweden (Väänänen, 1989; Hiltunen, 1982). The Kaunisvaara Greenstone Group has been correlated with the aforementioned Veikkavaara and Kiruna Greenstone groups (Lindroos, 1974).

Based on this information all sedimentary carbonate samples from formations lying on

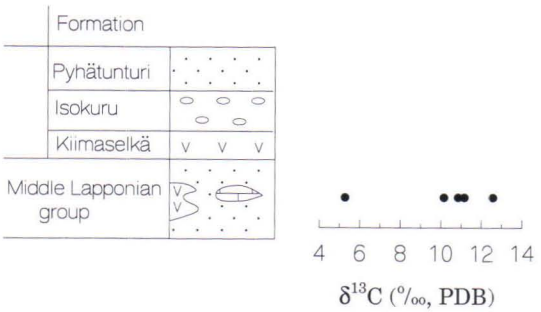

Fig. 32. Schematic stratigraphic column of the Pyhätunturi area. All sedimentary carbonate samples are thought to represent the Lapponian metasedimentary formations, which are stratigraphically below the Pyhätunturi, Isokuu and Kiimaselkä formations. Symbols as in Fig. 12.

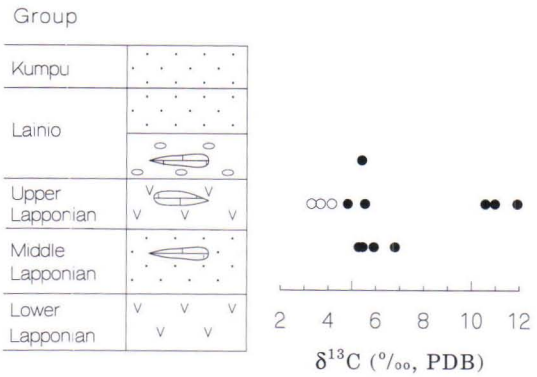

Fig. 33. Lithostratigraphy of the Central Lapland Complex in the Kittilä area modified from the general stratigraphic column presented by Lehtonen et al. (1992), showing variations in the $\delta^{13}C_{Tot}$ values of sedimentary carbonates through the stratigraphic succession. Open circles represent samples from the Rautuvaara Formation. Symbols as in Fig. 12.

top of different greenstone units would seem to represent approximately the same stratigraphic level.

$\delta^{13}C$ results

Pyhätunturi, Pelkosenniemi. The carbonate contents in the total carbonate fraction and the carbon and oxygen isotope compositions of samples from the Pyhätunturi area are listed in Table 10 and the $\delta^{13}C_{Tot}$ values with respect to the stratigraphic column are shown in Fig. 32. All these sedimentary carbonate samples are highly enriched in ^{13}C, and the mean $\delta^{13}C_{Tot}$ value is 10.0±2.8‰. However, taking into account the uncertainty in the stratigraphic interpretation of the Pyhätunturi succession discussed above, more studies are needed from the Pyhätunturi area in order to ascertain the stratigraphic position of the Kiimaselkä, Isokuru and Pyhätunturi formations with respect to the ^{13}C-enriched carbonates.

Kittilä–Kolari. The carbonate contents in the total carbonate fraction and the carbon and oxygen isotope ratios of the sedimentary carbonate samples from the Kittilä–Kolari area are listed in Table 10 and shown together with the stratigraphic column in Figure 33.

Carbon isotope results (Table 10) show that all sedimentary carbonates in this area are either moderately or strongly enriched in ^{13}C. The Middle Lapponian dolomites from Kuoninkivaara show a mean $\delta^{13}C_{Tot}$ value of 5.9±0.7‰. In the predominantly volcanic Upper Lapponian Group the mean $\delta^{13}C_{Tot}$ value is 8.8±3.3‰ for the Riikonkoski-Aakenustunturi area and 3.7±0.4‰ for samples from the Rautuvaara Formation in the Kolari area. Furthermore, the only analysis representing the Lainio Group (C-179, Luosujoki) is moderately enriched in ^{13}C showing a $\delta^{13}C_{Tot}$ value of 5.4‰.

Karasjok–Kittilä. The dolomite contents in the total carbonate fraction and the carbon and oxygen isotope ratios of samples from the southern part of the Karasjok-Kittilä Greenstone Belt are given in Table 10 and illustrated in Figure 34 relative to the stratigraphic column.

In the Lower Lapponian sample from Madetkoski, Sodankylä (C-169-A) the $\delta^{13}C_{Tot}$ value of carbonate is -1.7‰. In the upper part of the Middle Lapponian Group the $\delta^{13}C_{Tot}$ values vary from 1.4 to 10.9‰ (Table 10; Fig. 34).

A stratigraphic drill core cross section

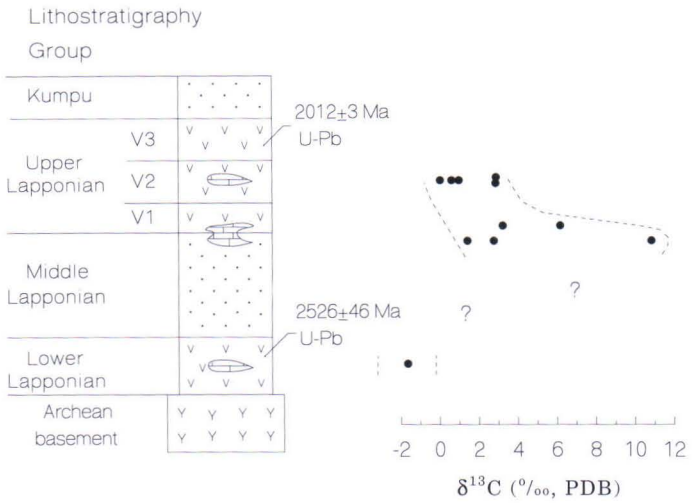

Fig. 34. Lithostratigraphy of the southern part of the Karasjok–Kittilä Greenstone Belt modified from the general stratigraphic column presented by Lehtonen et al. (1992), showing variations in the $\delta^{13}C_{Tot}$ values of sedimentary carbonates throughout the stratigraphic succession. V1, V2 and V3 denote three successive volcanic formations, namely the Sattasvaara Formation, the Kautoselkä Formation and the Vesmajärvi Formation, respectively. Symbols as in Fig. 12.

through the transition zone from the Middle Lapponian to the Upper Lapponian Group from the Rajala area in Sodankylä is shown in Fig. 35. Here the dolomite sample representing the lowermost carbonate bed in the section is associated with quartzites and displays the highest $\delta^{13}C_{Tot}$ value of 10.9‰. The other two samples were collected from higher in the sec-

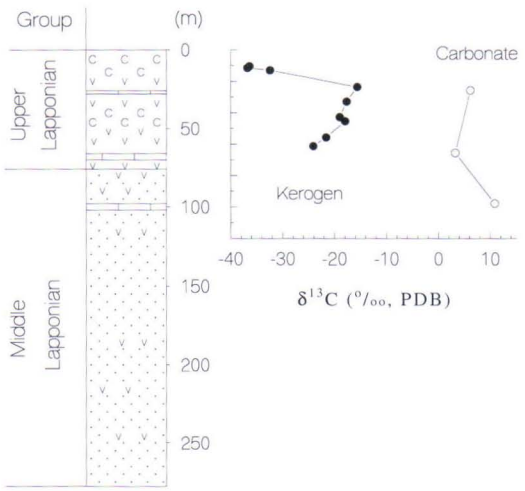

Fig. 35. Comparison of the $\delta^{13}C$ values of kerogen in black shales with $\delta^{13}C$ values of carbonate in sedimentary carbonate intercalations in a drill core section at Rajala, Sodankylä (C-305, Fig. 31). Stratigraphic column is simplified after J. Räsänen (pers. comm., 1993). The core intersects the transition from Middle Lapponian metasediments to Upper Lapponian ultramafic volcanics of the Karasjok–Kittilä Greenstone Belt. Symbols as in Fig. 12.

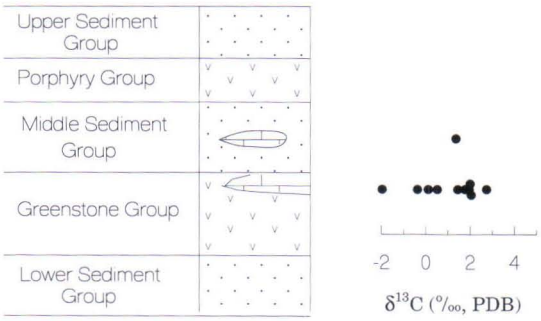

Fig. 36. General supracrustal stratigraphy in western Lapland according to Witschard (1984) also showing $\delta^{13}C_{Tot}$ values of carbonate in sedimentary carbonate formations. Most samples represent metasedimentary units in the upper part of the Greenstone Group, and only one sample has been collected from the Middle Sediment Group (Pahakurkkio Group). Symbols as in Fig. 12.

tion, above the lowest ultramafic units and are associated with graphitic schists, mica schists and volcanic rocks; their mean $\delta^{13}C_{Tot}$ value is 4.7±2.1‰. Judging from these results the stratigraphic section seems to record a transition from highly ^{13}C-enriched to moderately enriched sedimentary carbonates.

Five sedimentary carbonate samples from the Kautoselkä Formation of the Upper Lapponian Group have a mean $\delta^{13}C_{Tot}$ value of 1.5±1.3‰, which is within the normal range of values for sedimentary carbonate of any age.

Western Lapland. Dolomite contents in the carbonate fraction and the results of the isotopic analyses are given in Table 10 and shown with respect to the general stratigraphic column in Figure 36. The mean $\delta^{13}C_{Tot}$ value of sedimentary carbonates from the Greenstone Group is 1.0±1.4‰, which is almost identical to that analysed from the Tiankijoki sample of the Middle Sediment Group (Fig. 36) and also with the mean $\delta^{13}C_{Tot}$ value for carbonates of the Kautoselkä Formation in Finnish Lapland.

Age constraints

Kittilä–Kolari. On the southern side of the Sirkka Line the Middle Lapponian metasediments are in many places intruded by albite diabases about 2200 Ma old (Tyrväinen, 1983; Lehtonen et al., 1992). In the Riikonkoski–Aakenustunturi area hypabyssal intrusions among the Upper Lapponian volcanic rocks have yielded zircon ages less than 2100 Ma, such as for instance 2044±7 Ma for the Sätkänävaara albite diabase and 2060±4 Ma for the Riikonkoski albite gabbro (Lehtonen et al., 1992). Therefore, the deposition of highly ^{13}C-enriched carbonates in the Riikonkoski–Aakenustunturi area is constrained to have occurred before this time.

Karasjok–Kittilä. A Lower Lapponian felsic metavolcanic breccia from the Madetkoski Formation in Peurasuvanto has yielded a zircon U-Pb age of 2526 Ma (Pihlaja & Manninen, 1988). Ultramafic komatiites from the Karasjok area in Norway were dated by Sm-Nd method on whole rock samples by Krill et al. (1985) to be 2085±85 Ma old. These komatiites are considered to be equivalent to the ultramafic Sattasvaara Formation of the Upper Lapponian Group (Lehtonen et al., 1992), and accordingly, the large drop in the $\delta^{13}C$ values roughly at the base of the Sattasvaara Formation (see Figs. 34 & 35) may be approximated by that time.

A felsic porphyry from the Vesmajärvi Formation has given a zircon U-Pb age of 2012±3 Ma (Lehtonen et al., 1992), which indicates that the isotopically normal sedimentary carbonates of the Kautoselkä Formation were deposited before that time (see Fig. 34).

Western Lapland. The age of deposition of these sedimentary carbonates is not well constrained. Zircons from a diabase sill within the Kiruna Greenstone Group have been dated to 2.2 Ga by the U-Pb method (Skiöld, 1986), while Skiöld & Cliff (1984) reported a Sm-Nd mineral isochron of 1.93±0.05 Ga from the Kiruna greenstones. However, because this is based on secondary minerals, it does not necessarily indicate the time of emplacement of the volcanic rock (Skiöld, 1986). A definite minimum age for the sedimentary carbonates in this work is 1909±17 Ma, which is a U-Pb zircon age for a felsic volcanic rock from the Porphyry Group (Skiöld & Cliff, 1984).

Pechenga–Varzuga Belt

The Pechenga–Varzuga Belt is located in the Kola Peninsula, in the northeastern part of the Fennoscandian Shield. Geographically it is composed of two distinct supracrustal zones, namely the western Pechenga Belt and the eastern Imandra–Varzuga Belt (Fig. 1). They both contain a Paleoproterozoic supracrustal sequence covering a time period of several hun-

Table 10. Carbon and oxygen isotope data for samples from the Central Lapland region.

Sample	Location	Dol[1]	$\delta^{13}C$, ‰, PDB[2]			$\delta^{18}O$, ‰, SMOW[2]	
		wt. %	Tot	Cal	Dol	Cal	Dol
Pelkosenniemi area							
C-347-B	Kiimaselkä, Pelkosenniemi	96	5.28		5.42		13.36
C-220-A	Kalkkivaara, Pelkosenniemi	0		12.57		19.03	
C-220-B	Akankoski, Pelkosenniemi	0		11.15		15.46	
C-348-A	Pyhäjoki, Pelkosenniemi	100			10.15		17.20
C-348-B	Pyhäjoki, Pelkosenniemi	100			10.85		17.71
Kittilä-Kolari area							
Ylläs formation, Lainio group							
C-179	Luosujoki, Kolari	97	5.42		5.45		23.96
Upper Lapponian group							
C-153	Nirtsankuusikko, Kittilä	99	11.92		11.95		18.64
C-154	Telaköngäs, Kittilä	82	10.98	9.22	11.26	18.31	18.48
C-180	Aakenusjoki, Kittilä	16	10.57	10.49	11.34	15.71	15.24
C-282-1	Riikonkoski, Kittilä	100			5.55		15.15
C-282-3	Riikonkoski, Kittilä	100			4.82		14.63
Rautuvaara formation, Upper Lapponian group							
C-216	Äkässaivo, Muonio	92	3.68		3.84		20.46
C-227-A	Juurakkojärvi, Kolari	98	3.30		3.35		19.20
C-227-B	Juurakkojärvi, Kolari	98			4.15		19.12
Middle Lapponian group							
C-315-A	Kuoninkivaara, Sodankylä	100			5.29		11.32
C-315-B	Kuoninkivaara, Sodankylä	100			5.45		12.14
C-315-C	Kuoninkivaara, Sodankylä	100			5.92		11.44
C-315-D	Kuoninkivaara, Sodankylä	100			6.80		12.10

1) Weight-% dolomite in total carbonate by XRD,
2) Tot = Total carbonate, Dol = Dolomite, Cal = Calcite.

dred million years and furthermore, sedimentary carbonates are present at several stratigraphic levels.

The Pechenga–Varzuga Belt is considered to comprise the remnants of a distinct orogenic episode (Gaál & Gorbatschev, 1987), and the geologic evolution there can be expected to be largely independent of the progress of the Svecokarelian orogeny. Since the carbon isotope systematics of the Pechenga–Varzuga Belt are important for subsequent interpretation, the data on sedimentary carbonates reported by Karhu and Melezhik (1992) will be reviewed below.

Geologic setting

Pechenga. The Paleoproterozoic Pechenga Belt comprises a 10-km-thick supracrustal sequence, deposited in a time interval of over 400 Ma (Mitrofanov et al., 1991; Hanski, 1992). The succession is characterised by cyclical repetition of sedimentary and volcanic rocks, which can be divided into four formations (Fig. 37). Of these the Kuetsjärvi and Kolosjoki formations in the middle of the section contain well preserved, sometimes stromatolitic, limestone and dolostone interbeds (Ne-

Table 10. (continued).

Sample	Location	Dol[1]	$\delta^{13}C$, ‰, PDB[2]			$\delta^{18}O$, ‰, SMOW[2]	
		wt. %	Tot	Cal	Dol	Cal	Dol
Karasjok–Kittilä Greenstone Belt							
Kautoselkä Formation, Upper Lapponian group							
C-199-A	Jänesvaara, Kittilä	66	2.89	2.97	2.81	14.79	15.20
C-211-10	Saattopora, Kittilä	99	2.87		2.95		14.76
C-211-11	Saattopora, Kittilä	100			0.61		13.02
C-215	Välimaa, Sodankylä	100			0.03		13.75
C-250	Tarvasenvaara, Kittilä	0	0.99	1.02		16.26	
Sattasvaara Formation, Upper Lapponian group							
C-305-2	Rajala, Sodankylä	1		3.23		17.62	
C-305-3	Rajala, Sodankylä	97	6.17		6.23		14.89
Middle Lapponian group							
C-221	Käyläselkä, Pelkosenniemi	100			2.77		19.34
C-305-1	Rajala, Sodankylä	98	10.85		11.14		16.49
C-359	Linnunlaulumaa, Pelkosenniemi	1		1.42		19.96	
Lower Lapponian group							
C-169-A	Madetkoski, Sodankylä	97	-1.66		-1.66		13.13
Western Lapland area							
Middle Sediment group (Pahakurkio)							
C-238	Tiankijoki, Tärendö, Sweden	6	1.36	1.33		18.76	
Greenstone group							
C-121	Äkäsjoensuu, Kolari	0		-0.37		20.84	
C-157	Aittamaa, Kolari	0		0.52		21.62	
C-208-A	Mannakorpi, Muonio	81	-1.96	-2.37	-1.74	16.01	19.67
C-208-B	Mannakorpi, Muonio	1		0.11		14.16	
C-208-C	Mannakorpi, Muonio	96	2.74		2.79		21.48
C-236-A	Masugnsbyn, Tärendö, Sweden	100			1.77		20.75
C-236-B	Masugnsbyn, Tärendö, Sweden	100			1.96		20.86
C-237	Hietajoki, Tärendö, Sweden	99	1.44		1.48		21.92
C-239	Kivivaara, Lannavaara, Sweden	100	2.00		2.03		21.01
C-240	Huornaisenvuoma, Lannavaara	99	2.05		2.08		20.25

1) Weight-% dolomite in total carbonate by XRD,
2) Tot = Total carbonate, Dol = Dolomite, Cal = Calcite.

grutsa et al., 1986). On the other hand, the uppermost Pilgujärvi formation was deposited in deep water (Hanski, 1992), and it is not known to contain sedimentary carbonates; it is known mostly for the associated Ni-bearing intrusions and cogenetic ferropicritic volcanism.

The Kuetsjärvi and Kolosjoki formations have, on the basis of lithologic similarities, been correlated with the Jatulian group in Karelia (Negrutsa et al., 1986).

Imandra–Varzuga. The cyclic volcanic-sedimentary succession of the Imandra–Varzuga Belt resembles that in the Pechenga Belt, and was also deposited over a long time inter-

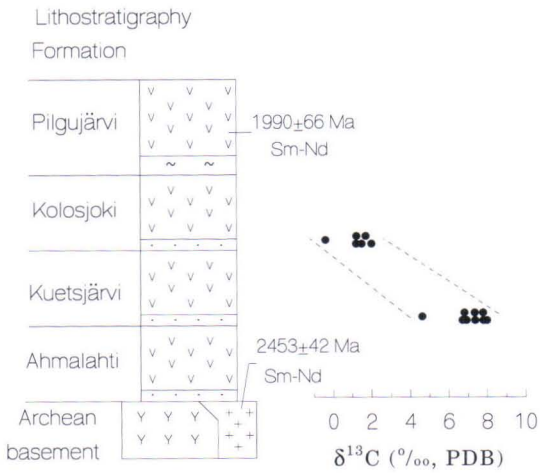

Fig. 37. $\delta^{13}C_{Tot}$ values of sedimentary carbonates from the Kuetsjärvi and Kolosjoki formations of the Pechenga Belt (Karhu & Melezhik, 1992). Lithostratigraphy is modified from Predovsky et al. (1987). The Sm-Nd whole rock-mineral isochron age for the Pilgujärvi formation is from Hanski et al. (1990), and the Sm-Nd isochron date for the Gora Generalskaya layered intrusion is given by Mitrofanov et al. (1991). Symbols as in Fig. 12.

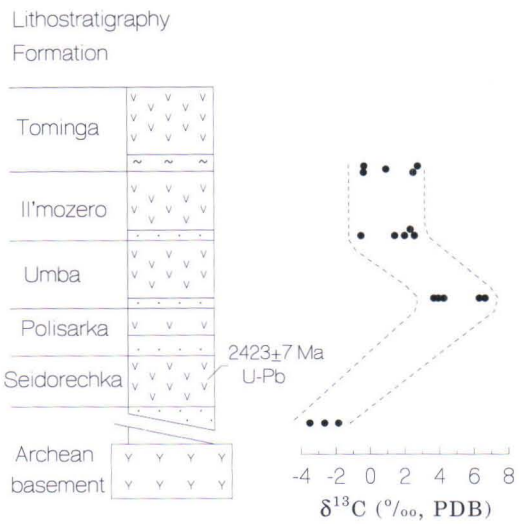

Fig. 38. $\delta^{13}C_{Tot}$ profile for sedimentary carbonates of the Imandra-Varzuga Belt (Karhu & Melezhik, 1992). Lithostratigraphic column has been modified from Predovsky et al. (1987). The U-Pb zircon date for the Seidorechka formation is from Mitrofanov et al. (1991). Symbols as in Fig. 12.

val spanning about 550 Ma (Mitrofanov et al., 1991). A partial, simplified stratigraphic column is shown in Figure 38, after Predovski et al. (1987).

The Seidorechka and Polisarka formations have been correlated with the Sumi–Sariolian group in Karelia (Gaskelberg et al., 1986). The overlying Umba and Il'mozero formations have been correlated with the Kuetsjärvi and Kolosjoki formations of the Pechenga Belt and also with the Jatulian group in Karelia (Zagorodnyi, 1980).

$\delta^{13}C$ results

According to isotopic results published by Karhu and Melezhik (1992), the mean $\delta^{13}C_{Tot}$ value of carbonate for samples from the Kuetsjärvi Formation of the Pechenga Belt is 7.0±1.0‰ and 1.2±0.8‰ for samples from the Kolosjoki Formation. In the Imandra–Varzuga Belt the corresponding mean values are -2.7±0.8‰ for the Seidorechka Formation, 5.0±1.4‰ for the Umba Formation, 1.6±1.2‰ for the Il'mozero Formation and 1.1±1.5‰ for the Tominga Formation.

The carbon isotope results are shown in Figures 37 and 38. The $\delta^{13}C$ values seem to vary systematically, and only one formation in each belt is characterized by ^{13}C-enriched carbonates.

Age constraints

The ^{13}C-enriched carbonates of the Kuetsjärvi Formation in the Pechenga Belt were deposited between 2453±42 and 1990±66 Ma (see Fig. 37). More importantly, the isotopically normal sedimentary carbonates of the Kolosjoki formation were evidently deposited before 1990±66 Ma.

The Seidorechka carbonates in the Imandra-

Varzuga Belt are older than 2423±7 Ma, and the ^{13}C-enriched carbonates of the Umba Formation are younger than this (see Fig. 38). Assuming that the correlation of the Tominga Formation of the Imandra–Varzuga Belt with the Pilgujärvi Formation of the Pechenga Belt is correct (see Zagorodnyi, 1980), the sedimentary carbonates of the Umba formation were also deposited before 1990±66 Ma.

$\delta^{13}C$ EVOLUTION OF SEDIMENTARY CARBONATES

Dating of metamorphosed sedimentary formations

For most of the Precambrian, where metazoan fossil remains are absent, the chronological correlation of sedimentary formations is almost totally dependent on radiometric age determinations. Generally radiometric dating methods are applied to igneous rocks, which may constrain the deposition time of a sedimentary formation either from below or from above. In the present discussion most estimates of depositional ages have been derived from these kinds of relationships.

In recent years new radiometric dating methods have been developed, and possibilities now exist for determining the depositional age of sedimentary rocks directly, even where they are metamorphosed. Such methods include the whole rock Pb-Pb method, which has occasionally been applied successfully to Precambrian sedimentary carbonate rocks (Moorbath et al., 1987; Jahn et al., 1990) and the Sm-Nd mineral isochron method using illite fractions from a weakly metamorphosed shales (Bros et al., 1992).

An attempt was also made in this study to date the Rantamaa Dolomite Formation in the Peräpohja area by the Pb-Pb method. However, the U contents of the Rantamaa dolomite turned out to be too low to cause any significant variation in the isotope ratios of Pb, and as a result, no meaningful ages could be obtained. Öhlander et al. (1992) experienced the same difficulties in the Kalix area, northern Sweden, and also obtained poor results due to insufficient variation in U/Pb ratios.

An additional dating method for determining the maximum age of clastic metasedimentary rocks is offered by recent advances in the analysis of U-Pb isotopes of single mineral grains particularly of zircon, using especially the ion microprobe. The youngest zircon in a sedimentary rock obviously gives the maximum depositional age for the sedimentary formation in question. Using this method Huhma et al. (1991) for example, were able to set very narrow limits for the timing of sedimentation of the Svecofennian graywackes.

$\delta^{13}C$ versus time curve: calibration

According to the data presented above, the isotopic composition of carbon in carbonate varies in a systematical way in the Paleoproterozoic sedimentary basins of the Fennoscandian Shield. Within individual carbonate units the dispersion of $\delta^{13}C$ values is generally rather limited, but successive stratigraphic units are often characterized by contrasting carbon isotope signatures. In addition, radiometric age determinations, reviewed in the preceding section, indicate that the deposition of ^{13}C-enriched carbonates was apparently restricted to a distinct time interval.

Therefore, it may be proposed that there exists a single $\delta^{13}C$ evolution curve which could explain the $^{13}C/^{12}C$ variations in different

Table 11. The mean $\delta^{13}C$ values of carbonate and estimated deposition times for selected supracrustal units from the Fennoscandian Shield.

	Formation	$\delta^{13}C$(TOT) mean ±1SD ‰, PDB	n	Estimated deposition time Ma#	Ref. to age*
1.	Madetkoski Formation Lower Lapponian Group	-1.7	1	2526±46	1)
2.	Seidorecha Formation Imandra–Varzuga Belt	-2.7±0.8§	3	2423±7	2)
3.	Sericite Schist Formation Kuusamo Schist Belt	8.1±0.1	2	2300–2206	3)
4.	Sompujärvi Formation Peräpohja Schist Belt	8.6	1	2300–2210	4)
5.	Misi dolomite formation Misi supracrustal belt	12.6±0.4	5	2300–2160	5)
6.	Lower Viistola Formation Kiihtelysvaara	10.0±0.7	5	2113±4	6)
7.	Jouttiaapa Formation Peräpohja Schist Belt	8.4±1.6	10	2090±70	7)
8.	Upper Petonen Formation Kuopio area	2.0±1.4	2	2062±2	6)
9.	Svecofennian Domain	0.8±1.1	52	1950–1890	8)

§) Results from Karhu & Melezhik, 1992,
*) References to age determinations: 1) Pihlaja & Manninen,1988, 2) Mitrofanov et al., 1991, 3) Silvennoinen, 1991, 4) Perttunen, 1991, 5) Patchett et al., 1981, 6)Pekkarinen & Lukkarinen, 1991, 7) Huhma et al., 1990, 8) see text.
#) ±deviations refer to uncertainty in radiometric age data.

supracrustal belts of the Fennoscandian Shield. Considering that our knowledge from Precambrian sedimentary sequences is at present fragmentary and incomplete, this kind of model cannot yet be proven. However, the model is easily testable and may be modified or rejected if conflicting isotope values arise.

For calibration of the age versus $\delta^{13}C$ curve, only those sedimentary carbonate units were selected for which the time of deposition could be estimated reasonably well from existing radiometric age data. The data set includes nine occurrences of sedimentary carbonates, for which the mean $\delta^{13}C$ value and the best estimate for the depositional age is given in Table 11 and illustrated in Figure 39.

The $\delta^{13}C$ values for carbonate from these sedimentary formations are mutually consistent, and they seem to define a systematic evolution trend for a time span of 600 Ma starting at the Archean-Proterozoic boundary. However, the evolution of $\delta^{13}C$ values from about 2400 to 2300 Ma is unknown, due to a lack of suitable sedimentary formations. For instance, the Sariolian sequences, which were possibly deposited at that time, are not known to contain sedimentary carbonate units.

The sedimentary carbonate formations deposited between about 2600 and 2400 Ma show $\delta^{13}C$ values of carbonate from -3 to -1‰ (Fig. 39). The two sedimentary units from this time period are the Madetkoski Formation of the Lower Lapponian Group from Peurasuvanto, Lapland (1) and the Seidorecha Formation of the Imandra–Varzuga Belt, from the Kola Peninsula, Russia (2). The isotope data for the

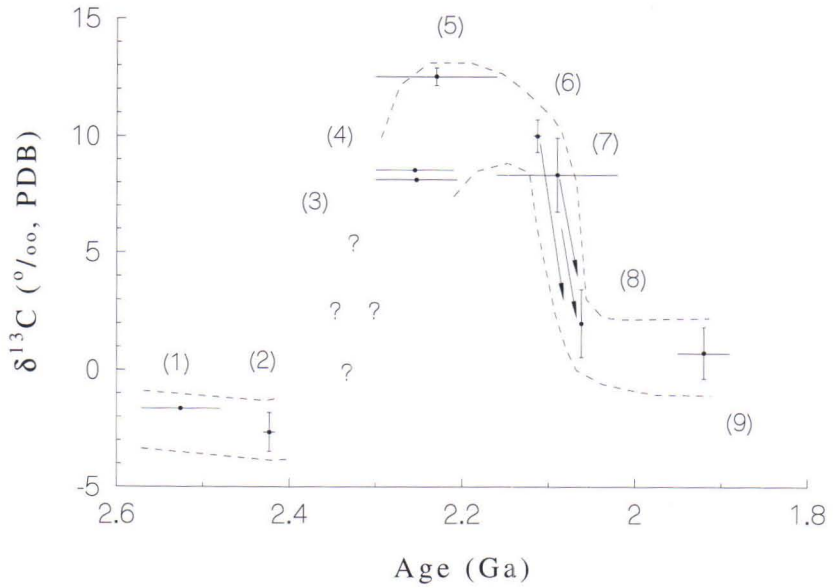

Fig 39. Evolution of the $\delta^{13}C_{Tot}$ composition of Paleoproterozoic sedimentary carbonates in the Fennoscandian Schield. Numbers refer to formations in Table 11. Arrows at about 2100–2060 Ma are combined to units, which are either preceded or followed by a relatively rapid, significant shift in the carbon isotope ratios.

latter formation was published by Karhu & Melezhik (1992).

The metasedimentary units intruded by ca. 2200 Ma metadiabase dikes are represented by two formations, namely the Sericite Schist Formation from the Kuusamo Schist Belt (3) and the Sompujärvi Formation from the Peräpohja Schist Belt (4). The minimum age of these units is defined by the diabase dikes, but the maximum age is set arbitrarily at the estimated time of formation of the pre-Jatulian weathering crust about 2300 Ma ago (e.g. Meriläinen, 1980; Heiskanen, 1992). The same applies also to the Misi dolomite formation (5), which was intruded 2160 Ma ago by a gabbro body. Although the maximum depositional ages for these formations are therefore not exact, they clearly indicate that ^{13}C-enriched carbonate sediments were already accumulating in the Fennoscandian Shield before 2200 Ma.

The extremely high average $\delta^{13}C$ value (12.6±0.4‰; Table 11) recorded for the Misi dolomite is not just a local curiosity, as similar average $\delta^{13}C$ values have also been recorded for the North Onega Subprovince (12.9±1.9‰, Table 2) and for the Siltstone and Kelloselkä formations at Salla and Kuusamo, respectively (12.4±0.4‰, Table 7).

Three sedimentary carbonate formations show evidence of a relatively rapid, 5–8‰ shift down from highly positive $\delta^{13}C$ values, as shown schematically by arrows in Figure 39. The lower Viistola Formation at Kiihtelysvaara (6) was deposited after the 2113 Ma lava flows of the Koljola Formation, which therefore provides a maximum age of deposition for these carbonates. The carbonate units within the upper Viistola and Petäikkö formations are characterized by decreasing $\delta^{13}C$ values (see Fig.12).

The volcanic Jouttiaapa Formation in the Peräpohja region lies between carbonate units of the Kivalo Formation and dolomite beds within the Kvartsimaa Formation, both of which show similar carbon isotope signatures (see Fig. 28). An average value coinciding with

the time of eruption of the Jouttiaapa basalts (2090±70 Ma) was therefore calculated from the Kivalo and Kvartsimaa samples. The drop in $\delta^{13}C$ values can be observed higher in the stratigraphy, in the Rantamaa Dolomite Formation.

In the Kuopio area the sedimentary carbonates of the Petonen Formation (8) display a decreasing $\delta^{13}C$ trend, which predates the extrusion of the volcanics of the Vaivanen Formation. These are correlated with the lithologically similar sequence from the Koivusaari Formation, for which an age of 2062±2 Ma has been obtained (see Figs. 16 & 18). The mean $\delta^{13}C$ value corresponding to this phase of volcanism was calculated using results from the uppermost samples from the Petonen Formation. One of these samples (C-192-G) was collected at a distance of 85 cm from the exposed contact and the other (C-177-B) represents a transitional contact with alternating carbonate and volcanogenic amphibole schist layers.

Additional, circumstantial support for a rapid decrease in the $\delta^{13}C$ values of carbonates between 2110 and 2060 Ma may be obtained from the Kuusamo area, where the decrease takes place within the Amphibole Schist Formation (see Fig. 26). There Silvennoinen (1991) suggested that the pyroclastic units of the Amphibole Schist Formation may have been related to the emplacement of the younger set of diabase dikes, dated at 2078±8 Ma.

Among formations overlying ^{13}C-enriched carbonates the earliest isotopically normal sedimentary carbonates represent the uppermost Petonen Formation at Kuopio (>2062±2 Ma, see Fig. 18). However, similar carbonates were also deposited elsewhere in the Fennoscandian Shield already before 2000 Ma. Examples are the Kautoselkä Formation from the Central Lapland region (>2012±3 Ma, see Fig. 34) and the Kolosjoki Formation from the Pechenga Belt (>1990±66 Ma, see Fig. 37). Furthermore, no sedimentary units of the Fennoscandian Shield deposited after 2060 Ma are known to contain ^{13}C-enriched carbonates, in agreement with the general $\delta^{13}C$ trend outlined in Figure 39.

It was shown earlier that the Svecofennian Domain (9) may be divided into provinces based on the carbon isotope ratios of carbonate (see Fig. 9). However, on the basis of existing geochronologic information, it is not possible to discern any differences in the depositional ages of these provinces. Therefore, all Svecofennian carbonate formations are here included together. The depositional age for these formations is constrained by data from detrital zircons, volcanic rocks and Svecokarelian synorogenic rocks as being between about 1950 and 1890 Ma, as was discussed earlier in this paper.

Comparison with other shield areas

Veizer et al. (1992a) studied the isotope geochemistry of three early Paleoproterozoic carbonate formations deposited between 2.5 and 2.0 Ga ago. This time interval is interesting, as it also corresponds to the age of the Karelian formations in the Fennoscandian Shield.

The formations studied (Veizer et al.,1992a) were the Malmani Dolomite of the Transvaal Supergroup, South Africa, the Duck Creek Dolomite of the Wyloo Group, Australia and the Espanola Formation of the Huronian Supergroup, Canada. From these three formations a total range in $\delta^{13}C$ compositions from -1.5 to 1.5‰ was measured.

The contrast in carbon isotope ratios between the results from sedimentary carbonates reported by Veizer et al. (1992a) and the Karelian carbonates of this study could reflect slightly different depositional ages. As is summarized by Veizer et al. (1992a) the estimated depositional ages for the Malmani Dolomite and the

Espanola Formation are 2300–2250 Ma and 2350±100 Ma, respectively, and they therefore are definitively older than most Karelian sedimentary carbonates. The age of the Duck Creek Dolomite is constrained to be within 2100±400 Ma, but due to the large age bracket any comparison with the Karelian formations is impossible.

Veizer et al. (1992b) reported $\delta^{13}C$ results from the 1.91 Ga old Coronation Supergroup in Canada, including samples from the Odjick, Rocknest and Cowles Lake formations. The $\delta^{13}C$ values vary from -2 to 2‰, although for marine components they report a smaller range, between 0 and 2‰. The depositional age of these formations is virtually the same as the age of the carbonate formations of the Svecofennian Domain, and in this case the carbon isotope signatures are almost identical.

Sedimentary carbonates enriched in ^{13}C have been reported from Paleoproterozoic formations in other shield areas, the most notable example being the Lomagundi Group in Zimbabwe (Schidlowski et al., 1976). Other examples have been reported from the Lewisian carbonates in Scotland (Baker & Fallick, 1989a), from the Einasleigh Metamorphics of the Georgetown Inlier, Australia (McNaughton & Wilson, 1983) and from the Francevillian Series in Gabon (Gauthier-Lafaye & Weber, 1989). Unfortunately however, the depositional ages of these units are generally not well constrained.

Sedimentary units of the Lomagundi Group were deposited after extrusion of Deweras lavas, which have yielded a Rb-Sr age of 2170±100 Ma (Hohndorf, unpublished data, in Treloar, 1988) and before a metamorphic event recorded in the K-Ar ages of 1905±70 Ma and 1974±70 Ma from Lomagundi slates (Vail et al., 1968). The Lewisian sedimentary carbonates in Scotland were metamorphosed at 1800 Ma, and the depositional age probably does not exceed 2100 Ma, as indicated by $^{87}Sr/^{86}Sr$ initial ratios and Sm-Nd crustal residence ages (see Baker & Fallick, 1989a). The deposition of the Einasleigh Metamorphics in Australia predate a metamorphic event at 1570±20 Ma (Black et al., 1979).

Subvolcanic N'Goutou intrusions in the lower part of the Francevillian Series in Gabon have been dated using the Rb-Sr isochron method as 2143±143 Ma (Bonhomme et al., 1982). Diagenetic clay fractions, acid leachates of these clays and the corresponding residues from black shales have yielded Sm-Nd isochron ages of 2099±115 Ma and 2036±79 Ma (Bros et al., 1992). These ages were interpreted as representing multi-episode illitization during early diagenesis, and the depositional age of these sequences therefore is similar to these estimates or slightly older.

On the basis of the age data presented above all these ^{13}C-enriched carbonates may have been deposited in the same time interval as the Karelian carbonates of the Fennoscandian Shield. However, due to poorly defined depositional ages none of them can be constrained to have been deposited exactly within the time period from 2200 and 2060 Ma, which includes most of the ^{13}C-enriched sedimentary carbonates from the Fennoscandian Shield (see Fig. 39). Therefore, at present there is no unequivocal evidence for a global $\delta^{13}C$ excursion at that time, although the data presented above as well as the results of this study from the Fennoscandian Shield strongly support that kind of model.

PROCESSES CONTROLLING $\delta^{13}C$ COMPOSITION OF SEDIMENTARY CARBONATES

Global carbon cycle

General

The long-term records of the carbon isotope ratios of sedimentary carbonates and organic matter are related to the operation of the global geochemical cycle of carbon which involves the transfer of carbon between the Earth's interior and the surficial reservoir (e.g. Holland, 1978, Chapter 6; Schidlowski & Aharon, 1992; Summons & Hayes, 1992). Here the surficial reservoir includes carbon in the atmosphere, biosphere, hydrosphere and unlithified sediments. The interior reservoir comprises carbon in sedimentary rocks and their metamorphic derivatives and carbon in the mantle.

The atmosphere, biosphere, hydrosphere and the unlithified sediments are also linked through important carbon transfer processes (e.g. Holland, 1978, Chapter 6). However, the time scales for these cycles are relatively short ($<10^4$ a), and for intervals exceeding about 10^5 a the surficial reservoir can be regarded as being in quasi-equilibrium and viewed as forming a unified system (Schidlowski & Aharon, 1992), as is shown schematically in Figure 40.

From the deep reservoirs carbon is transferred to the surficial system as a component in volcanic and metamorphic fluids and as a result of weathering processes (Holland, 1978, Chapter 6). Most of this carbon probably represents crustal carbon, although the proportion of juvenile carbon from the mantle is also significant (Des Marais, 1985). The $\delta^{13}C$ values of both these components are close to -5‰. For the mantle this is inferred from the $\delta^{13}C$ frequency distributions of carbonatites and diamonds. Carbonatites show very limited variability in the $\delta^{13}C$ compositions with a mean at -5.4‰, and this is comparable to the $\delta^{13}C$ values of most diamonds showing a major mode at -5.5‰

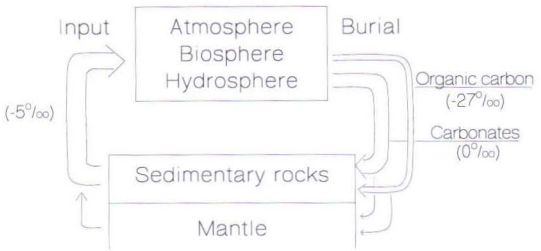

Fig. 40. Schematic representation of the global carbon cycle relevant at time scales $>10^5$ a. Numbers refer to $\delta^{13}C$ values of carbon, and indicate long-term average compositions (e.g. Schidlowski et al., 1983).

(Deines, 1992). An average $\delta^{13}C$ composition for carbon in the exogenic cycle has been calculated from inventories of various crustal reservoirs, and the results of these compilations range from -5.2 to -4.5‰ (Holser et al., 1988), indistinguishable from carbon of presumed mantle derivation.

The global carbon cycle is intimately coupled with the evolution of life and linked with cycles of other elements, most notably with the geochemical cycle of oxygen (e.g. Holland, 1978; Broecker, 1970). Isotopic records relating to the state of the ancient carbon cycle are therefore also of potential interest for understanding the evolution of the biosphere and the development of atmospheric oxygen levels.

Isotope fractionations within the global carbon cycle

The fractionation mechanisms are governed either by kinetic isotope effects, which depend on differences in the reaction or translocation rates between the heavy and light carbon isotope, or by thermodynamic exchange equilibria. Among these mechanisms kinetic isotope effects associated with carbon fixation by

autotrophic organisms are of primary importance.

In autotrophic carbon fixation carbon dioxide (CO_2) or dissolved bicarbonate (HCO_3^-) is assimilated by organisms as the immediate source of cellular carbon (see e.g. Chapman & Gest, 1983). These processes may proceed via different pathways, which are characterized by significant, though variable kinetic carbon isotope effects. They all lead to a marked enrichment of the light carbon isotope in the organic substance (e.g. Park & Epstein, 1960; Schidlowski & Aharon, 1992).

The quantitatively most important assimilation pathway is the C3 or Calvin cycle photosynthesis, which is operated for instance by algae, cyanobacteria and most plants. Apparently, it is responsible for the generation of the bulk of the present and fossil biomass of the Earth (Schidlowski & Aharon, 1992). The C3 photosynthesis involves a two step fractionation mechanism, originally described by Park & Epstein (1960). The average fractionation displayed by this pathway is close to -20‰ relative to atmospheric carbon dioxide, which indicates that the $\delta^{13}C$ value of the generated organic material will be around -27‰ with respect to the PDB standard in the presence of an atmoshere with a $\delta^{13}C$ composition at about -7‰ (Schidlowski & Aharon, 1992).

Carbon isotope fractionations associated with the surficial carbon dioxide-bicarbonate-carbonate system are only moderate when compared to the extensive kinetic effects accompanying the autotrophic carbon fixation. These fractionations are largely governed by chemical exchange equilibria between the reservoirs of atmospheric carbon dioxide ($CO_2(g)$), dissolved carbon dioxide ($CO_2(aq)$), bicarbonate ions (HCO_3^-) and precipitated carbonates.

The equilibrium fractionations between the various carbonate species depend on temperature. At low temperatures the calibrations presented by Emrich et al. (1970) and Mook et al. (1974) predict the following equilibrium order of ^{13}C-enrichment from the highest to the lowest:

$$CaCO_3\text{-}HCO_3^- \text{-}CO_2(g)\text{-}CO_2(aq).$$

At 25°C $CO_2(aq)$ is about 1‰ depleted and HCO_3^- about 8‰ enriched in ^{13}C relative to $CO_2(g)$. The fractionation between precipitated $CaCO_3$ and dissolved HCO_3^- is about 2‰. This indicates that carbonates follow relatively closely the isotopic composition of the dissolved bicarbonate, which is, and has always been, the dominant carbon reservoir in the atmosphere-biosphere-hydrosphere system (e.g. Holland, 1978, Chapter 6; Holser et al., 1988).

Mass and isotope balance constraints

In the absence of life all carbon entering the surficial system would be deposited as carbonates, and the $\delta^{13}C$ values of these carbonates would be the same as in the average supply (Broecker, 1970), or about -5‰. In the presence of life however, part of the carbon in the surficial reservoir is buried as organic matter, which is strongly depleted in ^{13}C relative to inorganic carbon due to the extensive fractionation associated with biological carbon fixation. In order to maintain the isotopic mass balance in the global carbon cycle, burial of ^{13}C-depleted organic carbon must be accompanied by deposition of carbonates with $\delta^{13}C$ values exceeding -5‰ (see Fig. 40).

This relationship may also be expressed in the form of an isotopic mass balance equation (Broecker, 1970; Schidlowski et al., 1983; Summons & Hayes, 1992)

$$\delta_i = f_{org}\delta_{org} + f_{carb}\delta_{carb}, \qquad \text{(Eq. 4)},$$

where δ_i represents the carbon isotopic composition of the average carbon input to the surficial system, f_{org} and f_{carb} are the fractions of the total carbon flux buried as organic matter and carbonates and δ_{org} and δ_{carb} represent the corresponding average carbon isotopic compositions.

By substituting $f_{carb} = 1 - f_{org}$ and denoting the

isotopic difference between the buried inorganic and organic carbon by $\Delta = \delta_{carb} - \delta_{org}$, solving for δ_{carb} in Equation 4 gives

$$\delta_{carb} = \delta_i + f_{org}\Delta. \quad \text{(Eq. 5)}$$

The equation shows that if we assume δ_i to be constant, the carbon isotopic composition of carbonate depends on the fraction of carbon buried as organic matter and on the difference in the isotopic composition of carbonate carbon and organic carbon. Moreover, if δ_{carb} and Δ are known and δ_i is assumed, then f_{org} can be determined.

Carbon burial through geologic time

It has been established that throughout geologic history the $\delta^{13}C$ values of carbonates have generally varied within relatively narrow limits around 0‰ (Schidlowski et al., 1983). There has been more variation in the $\delta^{13}C$ values of organic carbon, for which Schidlowski et al. (1983) suggested a mean value of -27±7‰. Using these values, it can be calculated (Eq. 5), that $f_{org} = 0.2$ or about one fifth of total buried carbon has been deposited as organic carbon.

When the long-term time trend in the $\delta^{13}C$ compositions of carbonates is studied in shorter time scales, the near constancy of the isotope values gives way to sequences of smaller scale oscillations (Schidlowski & Aharon, 1992). The existence of secular variations in the $\delta^{13}C$ values of Phanerozoic sedimentary carbonates was demonstrated by Veizer et al. (1980). The highest $\delta^{13}C$ values for the Phanerozoic occur in late Carboniferous and Permian sedimentary carbonates. Veizer et al. (1980) reported an average $\delta^{13}C$ value of 2.0‰ for the Permian, but at least locally and intermittently the $\delta^{13}C$ of carbonates exceeded 6‰ (Magaritz et al., 1983; Popp et al., 1986).

Systematically ^{13}C-enriched sedimentary carbonates have also been reported from Neoproterozoic successions of Svalbard, East Greenland and elsewhere (Derry et al., 1992; Knoll et al., 1986). These results show that carbonates with $\delta^{13}C$ values between 4 and 8‰ were deposited for much of the time between 900 and 600 Ma, with brief negative excursions, possibly associated with glacial periods (Derry et al., 1992).

In the study of Knoll et al. (1986) the isotopic composition of organic carbon was also analysed, in addition to carbonates. Based on the average analytical data (δ_{carb}=5‰, Δ=29‰) they calculated that the burial rate of organic carbon could have been doubled (f_{org}=0.34, Eq. 5). In order to transform the burial fraction of organic carbon to burial rate they assumed the modern value for the global total carbon burial. Compared to this example, the Paleoproterozoic carbon isotope shift recorded in the carbonates of the Fennoscandian shield appears to have been even more extreme.

Over a period of at least 100 Ma carbonates deposited in the Fennoscandian Shield were characterized by carbon with $\delta^{13}C$ values varying from about 8 to 12‰ (Fig. 39). Taking 10‰ as an average value for this time period and assuming that the difference has remained constant as 27‰, Equation (5) indicates that f_{org} would be 0.55. If it is assumed that this was a global event, then this implies that during this episode the burial rate of organic carbon would have exceeded the burial rate of inorganic carbon. Considering that the carbon cycle has generally remained within a rather well balanced dynamic equilibrium through most of Earth's history, it is not easy to understand what kind of conditions could cause such significant deviations.

Carbonate deposition in restricted environments

All the considerations presented above refer to carbonate depositional systems, which are open to the global oceans, in which the isotopic composition of carbon is buffered by the large reservoir of oceanic bicarbonate. However, in restricted basins exchange of carbon with the

global oceans may be unable to maintain isotopic equilibrium, and as a result the isotopic composition of dissolved bicarbonate may vary independently. In such environments voluminous burial of organic matter, for instance, may lead to local precipitation of carbonates enriched in ^{13}C. A similar mechanism was suggested by Schidlowski et al. (1976) as an explanation for the existence of the ^{13}C-enriched carbonates in the Paleoproterozoic Lomagundi Group of Zimbabwe.

Analogous situations may arise in anoxic diagenetic settings within sedimentary successions, where organic matter is decomposed by methanogenic processes. Methane generated under these conditions is highly depleted in ^{13}C, and may be accompanied by deposition of carbonates which are highly enriched in ^{13}C. However, the $\delta^{13}C$ values for these carbonates seem to vary widely. For instance Friedman & Murata (1979) analysed apparently methane- related dolomite samples from the Monterey Shale, and found a range of $\delta^{13}C$ values from 3 to 21‰. Similarly Deuser (1970) reported a range of $\delta^{13}C$ values from -64 to 21‰ for Quaternary methane-related dolomites from continental shelf settings.

Evidently, locally operating processes in restricted environments are able to produce conditions which lead to deposition of ^{13}C-enriched carbonates. Nevertheless, these mechanisms probably are not sufficent to explain the evolutionary trend of $^{13}C/^{12}C$ ratios presented in Figure 39. Firstly, the vast area covered by the ^{13}C-enriched carbonates cannot be considered as a single restricted basin. Secondly, based on age data and isotopic results the carbon isotope excursion appears to have lasted over 100 Ma, and during that time only ^{13}C-enriched carbonates were deposited. The areal extent, the duration and the systematical character of the carbon isotope pattern strongly suggest that the atmosphere and the global oceans were also involved. These considerations do not, however, exclude the possibility that some of these ^{13}C-enriched carbonate sequences were deposited in restricted basins. Essential is that even these basins apparently were in near equilibrium with the global oceans with respect to the isotopic composition of carbon.

Evidence from graphitic sediments

The Karelian carbonate formations are often associated with black shales. In the Kiihtelysvaara–Onega area the light-colored Jatulian quartzites and dolomites are separated from the darker, graphitic Ludian formations by a distinct facies boundary. The carbonate units around the domes of the Pitkäranta and Kuopio areas are also closely associated with graphitic schists, and the same is true for the dolomites of the Western Kainuu zone. Likewise, in the Kuusamo Schist Belt the Dolomite Formation is succeeded by the graphitic Amphibole Schist Formation. At Rajala, in the southern part of the Karasjok–Kittilä Greenstone Belt the lowest dolomite units are followed by a transition zone, were komatiitic pyroclastic beds alternate with carbonate layers and graphitic schist units.

Selected samples from these formations were analysed for their carbon isotope ratios and these results together with the carbon and sulfur elemental abundances are given in Table 12. Additional information including grid coordinates and brief descriptions are given in Appendix 2. For comparison, Table 12 also shows a few organic carbon analyses from carbonate rocks. The analysed carbonates are mostly well preserved, stromatolitic dolomites from greenschist facies environments.

Based on the stratigraphic position of the graphitic schist samples and evidence from radiometric age data, all these samples (Table 12) appear to represent the time period from about 2.11 to 2.06 Ga. Additional evidence is provided by the carbon isotope systematics of associ-

Table 12. $\delta^{13}C$ values of kerogen and the contents of C_{org} and S in black shales and dolomites.

Sample no.	Location (Drill core/Depth (m))	$\delta^{13}C$[1] ‰, PDB	C_{org} wt. %	S[2] wt. %
Black shales				
Juuka				
K-10-A	Petrovaara	-19.74	24.0	2.7
K-10-B	Petrovaara	-20.93	10.3	2.3
K-10-C	Polvela	-19.91	18.8	1.9
K-10-D	Polvela	-20.53	27.8	0.44
K-10-E	Polvela	-18.48	5.6	0.01
Kiihtelysvaara, Petäikkö Formation				
K-9-A	Viistola	-17.56	6.3	0.07
K-9-B	Viistola	-17.81	30.5	0.02
K-9-C	Hyypiä	-19.96	32.7	1.17
K-9-D	Hyypiä	-19.67	34.2	0.18
Lake Onega area, Ludian Group				
K-25	Sunga	-23.77	87.4	1.45
Kuusamo Schist Belt, Amphibole Schist Formation				
K-32	Kuivajärvi, Kuusamo	-16.62	8.2	0.01
K-100	Purnujärvi, Kuusamo	-17.00	0.94	0.26
Kuopio				
K-1	Laivonsaari, Kuopio	-30.08	50.5	1.92
Karasjok–Kittilä Greenstone Belt, mainly Middle Lapponian				
K-60	Miekkakoski, Savukoski	-21.91	5.6	6.11
K-63-1	Peurasuvanto, Sodankylä	-36.34	2.6	1.64
K-63-2	Peurasuvanto, Sodankylä	-38.07	3.7	<0.01
K-63-3	Peurasuvanto, Sodankylä	-43.55	9.2	0.02
K-63-4	Peurasuvanto, Sodankylä	-21.63	1.5	<0.01
K-65	Jeesiörova, Kittilä	-31.29	4.3	17.2
K-112-1	Rajala, Sodankylä (R3/10.4)	-36.38	1.7	1.05
K-112-2	Rajala, Sodankylä (R3/13.0)	-32.41	7.5	1.85
K-112-3	Rajala, Sodankylä (R3/23.6)	-15.61	2.2	0.74
K-112-4	Rajala, Sodankylä (R3/32.9)	-17.66	0.62	0.46
K-112-5	Rajala, Sodankylä (R3/45.7)	-17.94	6.8	0.32
K-112-6	Rajala, Sodankylä (R3/11.5)	-36.75	9.8	<.01
K-112-7	Rajala, Sodankylä (R3/55.7)	-21.59	13.6	1.42
K-112-8	Rajala, Sodankylä (R3/42.7)	-18.99	7.3	0.23
K-112-9	Rajala, Sodankylä (R3/61.2)	-24.11	8.8	0.69
Kerogen in carbonates				
K-22-A	Miihkailinmaa, Tervola (C-170-A)	-24.32 (11.13)	0.01	
K-22-D	Miihkailinmaa, Tervola (C-170-D)	-25.05 (9.63)	0.006	
K-24	Kalkkimaa, Tornio (C-212-B)	-18.99 (8.49)	0.01	
K-106	Kuetsjärvi Formation, Petschenga	-21.17 (7.34)	0.002	
K-107	S. Oleny Island, Onega area (C-349)	-21.32 (9.66)	0.02	

[1] Numbers in brackets give the $\delta^{13}C$ values for total carbonate.

[2] Sulfur determinations by R. Saikkonen with Leco analyser at the Geological Survey of Finland.

ated carbonates and the $\delta^{13}C$ evolution trend (Fig. 39).

The black shales associated with ^{13}C-enriched carbonates of the Fennoscandian Shield share some distinctive features. The carbon contents in them are exceptionally high, often exeeding 10%, but in contrast they appear to be generally almost competely devoid of sulfides. In this respect they are distinct from the slightly younger black shales from the about 1.97 Ga successions of the Kainuu–Outokumpu zone (Loukola-Ruskeeniemi, 1992), which are characterized by high contents of both sulfur and carbon (Fig. 41). The existence of the sulfur-rich and sulfur-poor types of black shales among the Paleoproterozoic formations of the Fennoscandian Shield was originally recognized by Melezhik (1985). Evidently, this geochemical feature is genetically significant, as is discussed in more detail below.

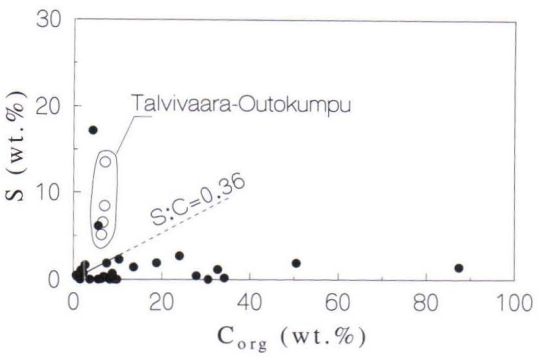

Fig. 41. Relationship between sulfur and organic carbon contents in black shales associated with the ^{13}C-enriched carbonates of the Fennoscandian Shield. For comparison are shown the line indicating the S/C ratio in modern normal marine sediments after Berner & Raiswell (1984) and the median values of representative analyses from black shales of the Kainuu-Outokumpu zone (open circles) as presented by Loukola-Ruskeeniemi (1992). Included are data from the Keretti and Vuonos mines at Outokumpu, and from the Talvivaara and Jormua occurrences in Kainuu..

Normal marine sediments of the present day oceans contain sulfur and carbon roughly in the ratio S/C=0.36, although this ratio has apparently varied through geologic time (Berner & Raiswell, 1983, 1984). Low S/C ratios in modern sediments are characteristic of lacustrine environments, where bacterial sulfate reduction is precluded due to the low sulfate levels in fresh waters. Therefore, it is possible that the sulfur-poor black shales of the Fennoscandian Shield were deposited under restricted conditions. Alternatively, pyrite formation may have been limited by iron availability, which is possible in sediments containing high concentrations of organic matter (Berner & Raiswell, 1984).

The geochemical pattern of carbon deposition during the Paleoproterozoic ^{13}C-excursion appears to be similar to that during the Late Carboniferous and Permian periods, when vast quantities of organic matter were accumulated in coal swamps. This was accompanied by a global positive shift in the $\delta^{13}C$ values of sedimentary carbonates, and according to model calculations, also atmospheric O_2 levels increased considerably during that time (Berner & Canfield, 1989). As a difference, the Late Carboniferous-Permian event is attributed to the rise of the vascular land plants, whereas organic carbon in Paleoproterozoic black shales obviously represents remains of microbial life.

The $\delta^{13}C$ values of organic carbon in the black shales of this study are generally between -21 and -17‰ (Table 12). The $\delta^{13}C$ values of associated carbonates range from about 3 to 10‰ (Tables 2, 3 and 7), and the apparent fractionation between organic and inorganic carbon remains close to 27‰. A slightly higher estimate was obtained from those dolomites for which the isotopic composition of both carbonate carbon and organic carbon was determined. The difference in the $\delta^{13}C$ values spans from 27.5 to 35.5‰, with an mean value at 31.4‰ (Table 12).

Some graphitic schists from the Karasjok–Kittilä Greenstone Belt are strongly depleted in ^{13}C, and show $\delta^{13}C$ values ranging down to -43‰ (Table 12). This unusually light organic carbon may be more than a local anomaly, as similar carbon isotope ratios have been reported for the Ludian black shales from the Lake Onega region (Chukhrov et al., 1984). The $\delta^{13}C$ values of carbon for the 9 samples in their data set range from -35.9 to-41.2‰. The exact

stratigraphic position of these samples relative to the ^{13}C-enriched carbonates is, however, not known.

In the Rajala area in Lapland the stratigraphic relationship between this unusually light carbon and ^{13}C-enriched carbonates can be observed in a drill core section (Table 12, R3). The core includes a transgressive profile from the upper part of the middle Lapponian quartzites and graphitic schists to pyroclastic komatiites of the Upper Lapponian Group (Fig. 35). Sedimentary carbonate beds are present only in the lower part of the section, and there the difference between the $\delta^{13}C$ values of inorganic and organic carbon is about 24‰. Higher up in the sequence carbonate units are absent and the $\delta^{13}C$ values of organic carbon record a dramatic drop from -15 to -37‰ within 10 meters. These results suggest that the light organic matter and the ^{13}C-enriched carbonates probably formed in the same sedimentary basin, but at different times or in different areas.

The stratigraphic sequence in the Rajala area in many respects resembles the Paleoproterozoic Francevillian quartzite black shale succession in Gabon, Africa, which is famous for its uranium ores and natural U reactors (Gauthier-Lafaye & Weber, 1989). The Francevillian Series has been dated to about 2.0 to 2.1 Ga using the Sm-Nd method on early diagenetic illite fractions (Bros et al., 1992). In addition, the Francevillian succession includes dolomite beds, in which the $\delta^{13}C$ composition of carbon varies from 2.6 to 6.3‰. The total organic carbon contents of the black shale units are high, from about 5 to 10%, and they show progressively more negative $\delta^{13}C$ values, starting from about -25 to a minimum of -46‰ higher up in the section (Gauthier-Lafaye & Weber, 1989).

The coexistence of a similar stratigraphic sequences with matching, unusual carbon isotope systematics in the Fennoscandian Shield and in Gabon suggest that the deposition of isotopically heavy carbonates could be partially related to concomitant deposition of unusually light organic matter.

Deposition of ^{13}C-depleted organic matter has also been reported from several Archean successions, where it has been attributed to production and utilization of biogenic methane (see Schidlowski et al., 1983; Hayes, 1983). Among natural carbon pools bacterial methane, produced in anoxic environments, is characterized by the lowest $\delta^{13}C$ values. This methane may be used and incorporated into biomass by methylotrophic bacteria, which in modern environments, however, are generally dependent on free oxygen, and therefore live in aerobic environments (Hayes, 1983).

Possible scenarios for a simultaneous existence of anaerobic and aerobic regions and their relation to the deposition of highly ^{13}C-depleted organic matter were discussed by Hayes (1983). He suggested that the anaerobic and aerobic regions were separated geographically, but not vertically. However, considering the new evidence from the roughly concomitant, transgressive succession in Gabon, in Lapland and in the Lake Onega area, the latter possibility appears more probable than the former.

Summary

The existing information concerning the timing and mutual relations of Paleoproterozoic sedimentary carbonates and kerogens is fragmentary. The results presented in this work nevertheless show that the roughly 2.2 to 2.1 Ga old sedimentary carbonates of the Fennoscandian Shield are systematically enriched in ^{13}C. In addition, isotopically similar carbonates are also found from other Paleoproterozoic shield areas, although exact chronostratigraph-

ic correlation is impossible at present due to the imprecision of existing isotopic age data.

The ^{13}C-enriched carbonate units are commonly but not always associated with voluminous organic carbon accumulations. An example of this is the Ludian group, which conformably overlies the Jatulian formations in the Kiihtelysvaara–Onega area. According to Walther's Law (Schoch, 1989) conformable facies boundaries, such as the one separating Jatulian and Ludian formations, are probably in general diachronous. Therefore, it is likely, that while Jatulian dolomitic stromatolite structures were forming in some parts of the basin, organic carbon was already accumulating in other, probably deeper parts of the same basin.

However, the voluminous organic accumulations in the Karelian sediments of the Fennoscandian Shield have only been recognized in strata that were evidently deposited at or around about 2.1 Ga or later. The existence of similar organic accumulations in the ^{13}C-enriched sedimentary carbonate formations older than this can, at the moment, only be inferred.

One conspicuous feature of the organic accumulations associated with heavy carbonates is the presence of separate black shale units characterized by unusually light, ^{13}C-depleted $^{13}C/^{12}C$ ratios. The exceptional depletions in ^{13}C have probably been produced in combined operation of methanogenic and methylotrophic bacteria. These cannot, however, be considered as representative of organic matter of that time in general, since most black shales in close association with ^{13}C-enriched carbonates show, in contrast, slight ^{13}C-enrichments relative to the average $\delta^{13}C$ value of -27‰.

All these considerations seem to indicate that a global event affecting the carbon cycle occurred in Paleoproterozoic time. Based on the evidence from associated organic accumulations the carbon isotope shift was probably caused by excessive relative burial of organic carbon, and the effect was enhanced by local burial of organic matter, strongly depleted in ^{13}C.

The net effect of the local burial of strongly ^{13}C-depleted organic matter would be to increase the average difference between the $^{13}C/^{12}C$ compositions of inorganic and organic carbon. The magnitude of this effect is difficult to estimate, since the two isotopically different organic components appear to have been deposited separately, and their relative proportions are not known.

If it is assumed that while carbonates having $\delta^{13}C$ values at 10‰ were being deposited, the corresponding average $\delta^{13}C$ composition of organic matter burial was -30‰, then the difference between these two would be 40‰. Substituting this figure for Δ in Equation 5 suggests a burial fraction (f_{org}) of 0.38, instead of 0.55 calculated above on the basis of Δ=27‰. Most probably the actual burial fraction of organic carbon was somewhere between these two figures, both of which are considerably higher than the modern burial fraction of about 0.2.

IMPLICATIONS FOR PALEOPROTEROZOIC SURFACE ENVIRONMENTS

The model presented above, which involves a large shift in the global, relative burial rates of organic carbon, also has some important implications for the behaviour of other elements. Conversely, these implications may also be used to empirically test the model, i.e. consequences and predictions of the model should be in agreement with geologic observations.

Autotrophic photosynthesis is the dominant source of oxygen in modern environments, and on the basis of geologic evidence this process has apparently been operating from the earliest Archean times (Schopf, 1993; Schidlowski & Aharon, 1992; Schidlowski et al., 1983). In this

process CO_2 is consumed and O_2 is liberated as a by-product, which may be represented by the general reaction:

$$CO_2 + H_2O \rightarrow CH_2O + O_2,$$

where CH_2O stands for carbon in newly formed organic matter. According to the stoichiometry of the reaction, for every mole of organic carbon produced, one mole of O_2 is liberated.

In biological processes majority of the dead organic material is reoxidized, which consumes also most of the oxygen, and the resulting CO_2 is returned back to the atmosphere-ocean system. Only a small fraction of the dead organic material is buried and preserved in sediments (Holland, 1978, Chapter 6), and the corresponding quantity of oxidizing potential is made available for the atmosphere-biosphere-hydrosphere system. This indicates that any increases in the burial rate of organic carbon will be accompanied by corresponding additions in the oxidizing potential.

The fractional burial rate of organic carbon could in theory be increased from 0.2 up to 1.0, which would mean transition to conditions where all carbon is deposited in the form of organic material. However, burial of organic matter also removes essential nutrients, like phosphorus and nitrogen, from the ocean, and thus the burial rate of organic carbon probably cannot be increased by more than a factor of 2 to 4 (Holland, 1978, Chapter 6). When the burial rate of organic carbon suddenly increases, the response time of the $\delta^{13}C$ composition of the dissolved bicarbonate in oceans is relatively short, being roughly between 10^5 and 10^6 a, while the atmospheric oxygen levels respond more slowly (Holland, 1978, Chapter 6; Kump & Garrels, 1986).

It was estimated above that in the period about 2.2 to 2.1 Ga ago the fractional rate of organic carbon burial was shifted to a value of between 0.38 and 0.55 depending on the value chosen to represent the average fractionation of carbon isotopes between carbonates and organic carbon at that time. Evidently this indicates a significant shift also in the redox balance of the surficial system.

To get an idea about the quantities in question, the effects of high relative burial rates of organic carbon may be modelled assuming the modern total burial rates for carbon, as was done for instance by Knoll et al. (1986) in the case of the Neoproterozoic carbon isotope excursion. Using the modern burial fraction of 0.2 and a total carbon burial flux of $28x10^{12}$ mol/a (Holland, 1978), the burial rate of organic carbon would be about $6x10^{12}$ mol/a, which is accompanied by liberation of an equivalent quantity of O_2 or other oxidized products. If the burial fraction is higher, between 0.38 and 0.55, the respective quantities of liberated O_2 will be from $11x10^{12}$mol/a to $15x10^{12}$mol/a. The amount of excess oxidizing potential accumulated within 100 Ma is equivalent to $5x10^{20}$–$9x10^{20}$mol O_2, which is from 12 to 22 times higher than the present inventory of O_2 in the atmosphere ($4x10^{19}$mol, Holland, 1978).

The calculation presented above indicates that the shift in the redox balance accompanying the positive carbon isotope excursion may have been considerable, although the magnitude of the increase in atmospheric O_2 levels remains unknown.

Several geological indicators are sensitive to atmospheric oxygen levels, one of these being the behavior of iron in ancient weathering crusts. At low oxygen levels iron is present as Fe^{2+}, which dissolves easily and is transported from the weathering profile. When the atmospheric oxygen contents increase over some threshold, iron will be oxidized, and it will be retained in the weathering crust as insoluble Fe^{3+} compounds (e.g. Holland, 1984, Chapter 7). The geochemical data for the oxidation state of paleosols was summarized recently by Holland (1992), and these data suggest a significant increase in the O_2/CO_2 ratio of the atmosphere between 2.2 and 1.8 Ga ago.

Other indicators suggesting considerable rise in the atmospheric oxygen levels at about 2.0

Ga are the formation of first red beds, the disappearance of the deposits containing detrital uraninite and pyrite (Holland, 1984, Chapter 7; Walker et al., 1983; Cloud, 1980) and the appearance of microfossils interpreted as eukaryotes (Han & Runnegar, 1992).

All these lines of evidence are compatible with a considerable increase in the atmospheric oxygen contents between about 2.2 and 1.8 Ga ago, although closer time constraints cannot be set due to the nature of the data. In this respect the carbon isotope records from sedimentary carbonates are important, as they suggest that the increase in the oxygen levels occurred largely between 2.2 and 2.1 Ga ago and that by 2.06 Ga ago the global carbon cycle was already shifted to lower, normal fractional burial rates of organic carbon.

The co-existence of ^{13}C-enriched carbonates and voluminous accumulations of sulfur-poor black shales is in general agreement with the model presented by Berner & Canfield (1989) for the evolution of the atmospheric O_2 during the Phanerozoic time. According to them the dominant factor, which has affected atmospheric O_2 levels and $\delta^{13}C$ values of dissolved bicarbonate in the oceans, is the redistribution of sediment between marine shales, non-marine coal basins and non-marine clastics. The model predicts that the highest Phanerozoic O_2 levels were reached as a result of the voluminous burial and preservation of organic matter in vast coal swamps during the Late Carboniferous and Permian times. As a difference, the coal basin sediments should in the Precambrian be understood as meaning sulfur-poor excessive accumulations of organic carbon, but otherwise the geologic settings appear similar.

IMPLICATIONS FOR THE KARELIAN SEDIMENTATION

General

The Paleoproterozoic carbon isotope record from sedimentary carbonates of the Fennoscandian Shield shows many systematic features that can be recognised in different parts of the shield. Where radiometric dating constraints exist these systematic variations can be described by the $\delta^{13}C$ evolution curve (Fig. 39). Within the Fennoscandian Shield the evidence supporting the general form of this $\delta^{13}C$ versus age curve is relatively strong, but indications of its global applicability are more theoretical.

It should be noted that the $\delta^{13}C$ versus age curve is a generalization that does not describe any small scale variations. It is also evident that local conditions may affect the carbon isotope ratios of carbonates. However, on the basis of all the evidence presented in this work, the $\delta^{13}C$ curve for sedimentary carbonates (Fig. 39) appears to be a useful stratigraphic tool in correlating sedimentary formations, as long as the caveats mentioned above are remembered.

Carbon isotope stages of the Karelian sedimentation

In order to interpret the evolution of the Karelian sedimentation, the $\delta^{13}C$ evolution curve (Fig. 39) is here divided into five stages, which are shown in Figure 42.

Stage I. The carbon isotope stage I includes the rare sedimentary carbonates which were deposited before the ^{13}C enrichment event. Presently available data come from the sedimentary horizons within the Lower Lapponian volcanic formations in Lapland and from the Imandra-Varzuga Belt in the Kola Peninsula. These formations appear to represent separate intracratonic rifting episodes.

Stage II. The second stage includes the shift

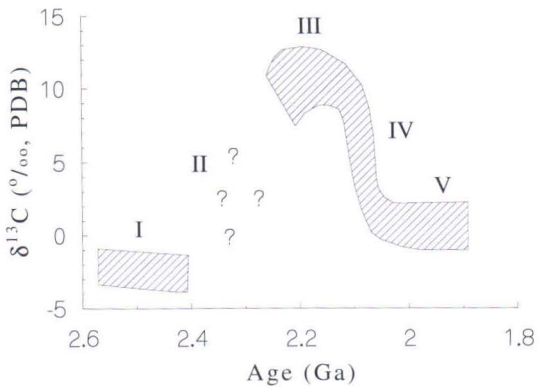

Fig. 42. Carbon isotope stages observed in Paleoproterozoic sedimentary carbonates of the Fennoscandian Shield.

in $\delta^{13}C$ values of carbonate from about 0 to about 10‰ (Fig. 42). This stage is hypothetical in the sense that no data sets have yet been analysed in which the increasing $\delta^{13}C$ trend could be seen. It is, however, possible, that the dolomite interbeds in quartzites deposited before the 2.2 Ga albite diabase sills and dikes could represent this stage, as the $\delta^{13}C$ values in these range from 5.3 to 8.6‰.

In many areas, including the Kuoninkivaara area in Central Lapland and the Sericite Schist Formation of the Kuusamo district, the siliciclastic sediments deposited before 2.2 Ga show tranverse cross bedding and other features suggestive of tidal origin (Nikula, 1988, Silvennoinen, 1992). These findings are important, because they show that at least some of these oldest ^{13}C-enriched carbonate samples are marine in origin. These formations appear to represent sedimentation on a stable epicontinental platform.

Stage III. The third stage contains the systematically ^{13}C-enriched sedimentary carbonates deposited on the Archean craton at about 2.2 to 2.1 Ga, in which the $\delta^{13}C$ values of carbonate vary from about 8 to 12.5‰ (Fig. 42). Sedimentary carbonate formations representing this stage are found in most Karelian supracrustal belts, except those that are located close to the western margin of the Archean craton.

As is clearly shown in the Kuusamo (Fig. 26) and Peräpohja (Fig. 28) cross sections, the formations of the carbon isotope stage III do not represent a single stratigraphic horizon, but rather have been formed in connection with successive rifting and sedimentation episodes on the epicontinental platform.

Some units representing stage III, such as the Kvartsimaa Formation of the Peräpohja Schist Belt (Figs. 27 and 28), contain sedimentary structures suggesting an intertidal environment (Perttunen, 1991), but other formations of stage III display mudcracks and other evidence of a supratidal origin (Perttunen, 1985 & 1991; Silvennoinen, 1972 & 1991).

Stage IV. Carbon isotope stage four records an approximately 10‰ drop in the $\delta^{13}C$ values of sedimentary carbonates. Evidence comes from various schist areas, and in several cases radiometric datings seem to constrain the event to the time interval between 2.11 and 2.06 Ga (see Fig. 39).

Sedimentary carbonates of this stage occur in most areas that contain Karelian supracrustal formations. In the Kiihtelysvaara–Onega region the uppermost Jatulian dolomite formations already show a decrease in the $\delta^{13}C$ values, which continues in the lowermost Ludian formations.

At the western margin of the Archean craton, in the southern part of the shield, only Stage IV carbonates are present. This appears to be true for the Pitkäranta, Varmonniemi, Kuopio, Ala-Siikajärvi and Western Kainuu areas. Further northwards this stage is represented by the Amphibole Schist Formation at Kuusamo, the Aatsinginhauta Formation in Salla, the Rantamaa Dolomite Formation in Peräpohja and the black shale unit between the middle Lapponian quartzites and the lowest ultramafic pyroclastics of the Upper Lapponian Group.

The position of the Lainio Group in the Kittilä–Kolari area is more problematical. Only one sedimentary carbonate sample has been analysed, and on the basis of a $\delta^{13}C$ value of 5.4‰, at least parts of the Lainio Group could

represent stage IV. This conclusion should nevertheless be confirmed with further isotopic studies.

Stage V. The youngest carbon isotope stage represents the period after about 2.06 Ga, when the $\delta^{13}C$ composition of sedimentary carbonates, according to all the evidence, remained in the range 0±3‰. In the Svecofennian Domain all sedimentary carbonates represent stage V. In the Archean Domain carbonates of stage V occur particularly in Lapland, where this stage includes all Upper Lapponian carbonates from the Kautoselkä Formation of the Karasjok–Kittilä Greenstone Belt and all carbonates from the greenstone belts in northern Sweden. This conclusion cannot however be generalized to embrace all carbonates in Swedish Lapland, as carbonates there probably occur at several stratigraphic levels, and only two levels in the upper part of the greenstone group were sampled for this work.

Classification of the Karelian formations based on carbon isotopes

With respect to the carbon isotope ratios of sedimentary carbonates there are two principal types of Karelian supracrustal successions, characterized by distinct carbonate depositional histories. The first, cratonic kind of sequence occurs well within the Archean craton (Fig. 43). It is characterized by a long deposition history of siliciclastic sediments, overlain by stage II and III dolomites, which, in turn, in most areas are followed by the deposition of stage IV limestones and dolomites.

A typical example of the cratonic sequence is the Kiihtelysvaara–Onega region. There the Sariolian and lower Jatulian siliciclastic metasediments are overlain by accumulations of upper Jatulian stage III dolomites up to hundreds of meters thick, followed by Jatulian and Ludian sedimentary carbonates representing stage IV. Similar overall successions are found for instance in the Kuusamo and Peräpohja schist belts and in the Central Lapland area.

The second kind of Karelian supracrustal successions is found close to the southwestern margin of the Archean craton, and is therefore here called the marginal type of sequence (Fig. 43). Characteristic of these formations is the presence of stage IV carbonates and the absence of carbonates representing earlier stages. The transition from cratonic to marginal sequences is abrupt, occurring within a few tens of kilometers (Fig. 43), and no transitional successions have been recognized.

An example of the marginal sequences is found around the Archean basement domes of the Pitkäranta area. There the sedimentary carbonates representing stage IV have been deposited directly on the Archean basement (Figs. 15 and 17), which indicates a preceding period of erosion. The Karelian successions in the Kuopio, Ala-Siikajärvi and Western Kainuu areas also show carbon isotopic signatures of stage IV, but, in contrast to the Pitkäranta area, carbonate beds there are underlain by siliciclastic metasediments. However, compared to the cratonic sequences the thickness of these formations remains relatively small. In the Western Kainuu zone the lower boundary of these quartzites, belonging to the Eskosenvaara Formation, is interpreted as an unconformity (Laajoki, 1991), but in the Kuopio area no unconformities have been reported from within the sequence.

The association of the sedimentary carbonates of the Kalix Greenstone Belt with stage IV is more tenuous. Firstly, the $\delta^{13}C_{Tot}$ values there are increasing rather than falling (Fig. 30). Secondly, the depositional basement is not known (Lager & Loberg, 1990), and, consequently, stage III carbonates might exist below the known part of the section.

On the other hand the sedimentary carbonate formations of the Kalix area also share some features typical of the marginal sequences. The measured $\delta^{13}C_{Tot}$ values range from 2.6 to 4.8‰

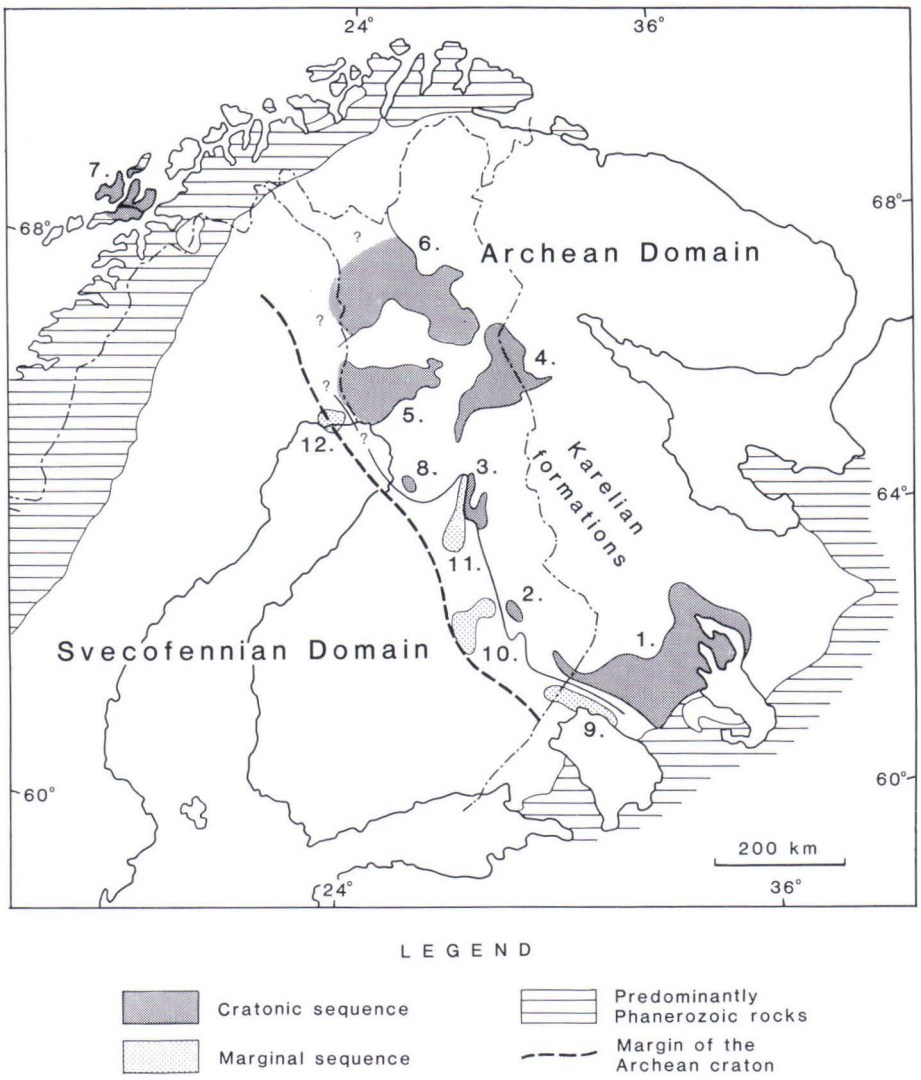

Fig. 43. Distribution of cratonic and marginal types of Karelian sequences based on interpretation of carbon isotope data. The cratonic sequences are: 1. Kiihtelysvaara–Onega, 2. Juuka, 3. Eastern Kainuu, 4. Kuusamo–Salla, 5. Peräpohja–Misi, 6. Central Lapland, 7. Lofoten–Vesterålen, 8. Pitkäselkä, Muhos, and the marginal sequences are: 9. Pitkäranta–Varmonniemi, 10. Kuopio–Ala-Siikajärvi, 11. Western Kainuu, 12. Kalix.

(Table 9), which are for instance comparable with results from the Pitkäranta, Kuopio and Western Kainuu areas (Tables 4 and 6). In addition, only minor quartzitic units are present, and the carbonate bearing Middle Group is separated from the Lower Group by an unconformity and a paleoweathering crust (Lager & Loberg, 1990).

As is suggested by the geographical distribution of the Karelian marginal sequences (Fig. 43) and other geological features described below, the deposition of the Karelian marginal sequences may have been related to break-up of the Archean craton and opening of a marginal basin during carbon isotope stage IV. This suggestion agrees with a recent esti-

mate of Kohonen & Marmo (1992), who suggested that the break-up of the continent occurred about 2.1–2.2 Ga ago.

Continental break-up is generally considered to be preceeded by mantle upwelling and doming (Burke & Dewey, 1973). On the surface this would be presented by a period erosion, such as appears to be typical of most Karelian marginal sequences. Early rifting is followed by opening of an oceanic basin and thermal subsidence of the margins. In the sedimentary sequences this would be seen as a transgressive shift from shallow water to deep water sedimentation. The stratigraphic successions in the Karelian marginal sequences are in accord with this model, as the Jatulian and Ludian successions there are followed by deeper water mica schists of the Kalevian group.

The boundary between marginal and cratonic sequences (see Fig. 43) follows the line drawn by Laajoki (1991) to separate Eastern and Western Karelides in the North Karelia and Kainuu areas. On the basis of lithological differences he further suggested that these crustal units may be mutually exotic. According to alternative solution presented above, the marginal sequences were possibly deposited in a different geotectonic environment, where the erosion-deposition history was dominated by processes leading to break-up of the Archean craton. Nevertheless, in the light of existing data it appears difficult to disprove either of these models.

Summary

The interpretations presented above are generally in agreement with the existing isotopic age data, and in many respects they conform to existing conceptions about the general stratigraphy of the Karelian formations. Nevertheless, even widely separated and lithologically different successions may be compared, and as a result new interpretations also arise. Some of these correlations are summarised and discussed shortly in the following.

Sedimentary carbonates of stage IV appear to be most interesting for the purpose of correlation. In eastern Karelia, in the middle of the Archean craton the transition from stage III to stage IV carbonates occurs roughly at the Jatulian-Ludian boundary, and therefore, the distinction between these groups has been evident from the turn of the century (e.g. Ramsay, 1902 &1906; Metzger, 1924; Sokolov, 1980). At the western margin of the Archean craton this boundary, however, cannot be easily recognised, and accordingly no distinction has generally been made between the Jatulian and Ludian sedimentary carbonates. Therefore, the recognition of the marginal type of Karelian sequences, characterized by stage IV carbonates, can be expected to be useful for future correlations.

Another interesting correlation possibility arises between widely separated formations in Lapland and those in the Kiihtelysvaara–Onega region. The sedimentary carbonates within the Middle Lapponian quartzites generally represent carbon isotope stage III and are therefore correlative with the Jatulian formations in Karelia. This also applies to similar carbonate units closely associated with volcanic formations in the Kittilä–Kolari region. However, carbonates from the voluminous volcanic formations in the southern part of the Karasjok–Kittilä Greenstone Belt as well as from the greenstone belts of Western Lapland represent stage V and therefore, these volcanic formations are apparently correlated with the Ludian formations in the Kiihtelysvaara–Onega region.

CONCLUSIONS

It has been shown that the Paleoproterozoic sedimentary carbonates show consistent evolutionary trends of $^{13}C/^{12}C$ ratios in different supracrustal belts of the Fennoscandian Shield. The timing of systematic isotope shifts was estimated using information from formations for which the age of deposition was constrained from radiometric data. The results suggest that in the time period 2.2 to 2.1 Ga only strongly ^{13}C-enriched carbonates, with $\delta^{13}C$ values in the range 10±3‰, were deposited. The carbonates deposited between 2.11 and 2.06 Ga recorded a sharp approximately 10‰ drop in the $\delta^{13}C$ values. Based on the systematics of this time trend and on the data from associated organic carbon accumulations the following conclusions can be made:

1. The data presented in this study as well as published results from the other shield areas are compatible with a model of a global perturbation in the carbon cycle, which was caused by excessive relative rates of burial of organic carbon.

2. The whole atmosphere-biosphere-ocean system was affected, as is evidenced by concomitant deposition of black shales characterized by heavier than normal carbon isotope ratios. Local deposition of isotopically unusually light organic carbon showing $\delta^{13}C$ values down to -43‰ may have enhanced the positive isotope shift of the surficial carbon reservoir.

3. As organic carbon burial is associated with oxygen production, the isotope shift may be connected with the generally observed rise in atmospheric oxygen contents at about 2.0 Ga. Based on carbon isotopic records from sedimentary carbonates this change probably occurred largely between 2.2 and 2.06 Ga ago.

4. The carbon isotope shift in carbonates may be used for stratigraphic correlation of sedimentary formations, at least within the Fennoscandian Shield.

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Appendix 1. Descriptions and locations of sedimentary carbonate samples.

Sample no.	Table no.	Original sample no.	Description	Yield[&]	Grid coordinates x	Grid coordinates y	Source[*]
C-7	1	383	Coarse-grained, white marble	9.46	6688.	1571.	7
C-14	1		Sheared, white marble	6.77	6694.26	2479.35	
C-65-A	1		Coarse-grained, white marble	9.42	6770.2	3563.8	7
C-65-B	1		Coarse-grained, light gray marble	8.99	6770.2	3563.8	4
C-65-C	1		Coarse-grained, blue marble	9.05	6770.2	3563.8	7
C-66-B	1		Medium-grained, gray marble	9.52	7005.7	2500.7	4
C-66-C	1		Medium-grained, white marble	9.46	7005.7	2500.7	33
C-67-A	1	2346	Medium-grained, salmon pink marble	9.19	6683.3	2577.1	7
C-67-B	1		Coarse-grained, salmon pink marble	8.53	6683.3	2577.1	15
C-67-C	1		Coarse-grained, salmon pink marble	9.09	6683.3	2577.1	15
C-67-D	1		Coarse-grained, pink marble	8.78	6683.3	2577.1	15
C-67-E	1		Medium-grained, white dolomitic marble	9.49	6683.3	2577.1	15
C-69	1	2348	Medium-grained, light gray marble	9.24	6938.7	1576.1	7
C-70-A	1	2352	Coarse-grained, white marble	9.64	6688.	1571.	7
C-70-B	1		Very coarse-grained, white marble	9.72	6688.	1571.	4
C-70-C	1		Coarse-grained, white marble	9.54	6688.	1571.	
C-72	8		Gray, siliceous, dolostone associated with columnar stromatolites	7.94	7327.6	2513.4	24
C-80	5	2365	Fine-grained, dark gray dolostone	9.81	7227.8	3444.4	7
C-81	8	2367	Fine-grained, white dolostone rock	9.68	7363.	3451.	7
C-116	8		Very finely crystalline, white dolostone, associated with stromatolites	9.10	7318.5	2522.0	24
C-117	1		Coarse-grained, white marble	9.74	6665.5	2437.2	
C-118	1		Very coarse-grained, white marble	9.44	6673.2	2491.2	30
C-119-A	1		Medium-grained, white marble	8.40	6683.9	2504.0	30
C-119-B	1		Coarse-grained pink marble	9.49	6683.9	2504.0	30
C-119-C	1		Very coarse-grained, white marble	9.56	6683.9	2504.0	30
C-119-D	1		Coarse-grained, white dolomitic marble	10.54	6683.9	2504.0	30
C-120-A	5	OKU-659	Fine-grained, gray dolostone	8.47	6957.2	4447.6	31
C-120-B	5	OKU-659	Fine-grained, gray dolostone	8.51	6957.2	4447.6	31
C-121	10		Medium-grained, gray marble	9.53	7484.9	2485.1	4
C-122-A	1		Medium-grained, light gray marble	10.13	6856.5	1538.5	4
C-122-C	1		Medium-grained, yellowish marble	9.19	6856.5	1538.5	
C-123-B	1		Medium-grained, light gray marble	9.78	6772.5	2426.7	4

[&] Total yield of CO_2 as µmol/mg. For pure calcite and dolomite the yields are about 10.0 and 10.8 µmol/mg, respectively.

[*] Source of samples: 1. E. Ekdahl, GSF, Kuopio, 2. J. Hallikainen, Lapin Marmori Oy, Loue, 3. E. Hanski, GSF, Rovaniemi, 4. R. Harinen, Partek Minerals Oy, Parainen, 5. M. Havola, GSF, Kuopio, 6. M. Honkamo, GSF, Rovaniemi, 7. P. Karhunen, Mineralogical Museum, GSF, Espoo, 8. R. Kesola, GSF, Kuopio, 9. J. Kohonen, GSF, Espoo, 10. A. Kontinen, GSF, Kuopio, 11. J. Kurki, Outokumpu Oy, Outokumpu, 12. I. Lager, Luleå University, Sweden, 13. M. Lehtinen, Partek Minerals Oy, Lappeenranta, 14. M. Lehtinen, Geological Museum, University of Helsinki, 15. P. Lehtinen, Lohja Oy, Sipoo, 16. M. Lehtonen, GSF, Espoo, 17. H. Lukkarinen, GSF, Kuopio, 18. T. Manninen, GSF, Rovaniemi, 19. P. Medvedev, Russian Academy of Sciences, Petrozavodsk, 20. D. Mihailova & K. Stepanov, Sevzapgeologija, St. Petersburg, Russia, 21. V. Niiniskorpi, SG Ab, Kiruna, Sweden, 22. J. Paavola, GSF, Kuopio, 23. Y. Pekkala, GSF, Espoo, 24. V. Perttunen, GSF, Rovaniemi, 25. P. Pihlaja, GSF, Espoo, 26. J. Räsänen, GSF, Rovaniemi, 27. P. Rastas, GSF, Rovaniemi, 28. J. Reinikainen, GSF, Espoo, 29. R. Ruotsalainen, National drill core archives, GSF, Loppi, 30. R. Saikkonen, Lohja Oy, Lohja, 31. R. Sarikkola, Outokumpu Oy, Outokumpu, 32. H. Schöberg, Swedish Museum of Natural History, Stockholm, 33. E. Sonninen, University of Helsinki, 34. V. Suominen, GSF, Espoo, 35. E. Tamminen, University of Oulu, 36. M. Torssonen, GSF, Espoo, 37. J. Väänänen, GSF, Rovaniemi, 38. A. Vorma, GSF, Espoo, (GSF = Geological Survey of Finland).

Appendix 1. (continued)

Sample no.	Table no.	Original sample no.	Description	Yield[&]	Grid coordinates x	Grid coordinates y	Source[*]
C-123-C	1		Medium-grained, yellowish marble	9.47	6772.5	2426.7	
C-125-A	1		Coarse-grained, white marble	9.59	6870.4	4448.8	13
C-125-B	1		Coarse-grained, white marble	9.41	6871.15	4447.94	13
C-127-A	4		Medium-grained, white marble	9.63			7
C-127-B	4	983	White marble with darker intercalations	9.33			14
C-128-1	8		Very finely crystalline, yellowish dolostone	9.09	7347.2	2542.4	2
C-128-2	8		As C-128-1	9.77	7347.2	2542.4	2
C-128-3	8		Very finely crystalline dolostone, associated with stromatolites	8.03	7347.2	2542.4	24
C-129	8		Fine-grained, gray, tremolite bearing dolostone	7.75	7320.	2505.	2
C-130	8		Very finely crystalline, white, dolostone	10.27	7327.6	2522.5	2
C-131	5		Fine-grained, gray marble	9.50	6871.4	4497.65	13
C-132-A	1		Medium-grained, white marble	9.06	6885.1	3521.6	13
C-132-B	1		Medium-grained, yellowish marble	8.34	6885.1	3521.6	13
C-133	2	2369	Medium-grained, carmine red dolostone	9.56			7
C-135-A	3	JuPe-11/20.10	Fine-grained, light gray marble	9.68	7001.66	4453.63	11
C-135-B	3	JuPe-21/18,00	Light gray, tremolite bearing marble	9.79	7001.64	4453.28	11
C-139	4	21B-HMM-78	Medium-grained, white marble	9.21	7001.80	3511.16	17
C-144	2	2172/Ramsay	Finely crystalline, gray dolostone	8.51			14
C-146	2	1255/Ramsay	Medium-crystalline, white dolostone	10.15			14
C-147	4	11-6-HJL-85	Fine-gr., white dolostone, 12.5 m from the Petonen–Vaivanen formation boundary	8.78	6980.28	3529.70	17
C-148	4	15-2-HKÅ-82	Medium-grained, white dolostone	9.22	6990.57	3529.91	17
C-149	4		Fine-grained, dark gray dolostone	9.59	7011.58	3569.22	22
C-150	2	3/Wahl	Finely crystalline dolostone	9.63			14
C-151	2	1306/Wahl	Fine-grained, white dolostone	9.68			14
C-152	2	1308	Fine-grained, light gray limestone	9.43			14
C-153	10	34A-ROK-74	Medium-grained, white marble	9.77	7510.60	2524.44	27
C-154	10	26A-PPR-75	Medium-grained, pink marble	8.85	7511.02	2535.47	27
C-156-A	6	43A-VH-70	Very finely crystalline, gray carbonate rock	8.28	7144.65	3530.70	10
C-156-C	6		Laminated carbonate rock, pelitic intercalations	9.63	7146.13	3532.65	10
C-157	10	51-JTV-78	Medium-grained, gray marble	9.27	7486.86	2484.89	37

[&] Total yield of CO_2 as µmol/mg. For pure calcite and dolomite the yields are about 10.0 and 10.8 µmol/mg, respectively.

[*] Source of samples: 1. E. Ekdahl, GSF, Kuopio, 2. J. Hallikainen, Lapin Marmori Oy, Loue, 3. E. Hanski, GSF, Rovaniemi, 4. R. Harinen, Partek Minerals Oy, Parainen, 5. M. Havola, GSF, Kuopio, 6. M. Honkamo, GSF, Rovaniemi, 7. P. Karhunen, Mineralogical Museum, GSF, Espoo, 8. R. Kesola, GSF, Kuopio, 9. J. Kohonen, GSF, Espoo, 10. A. Kontinen, GSF, Kuopio, 11. J. Kurki, Outokumpu Oy, Outokumpu, 12. I. Lager, Luleå University, Sweden, 13. M. Lehtinen, Partek Minerals Oy, Lappeenranta, 14. M. Lehtinen, Geological Museum, University of Helsinki, 15. P. Lehtinen, Lohja Oy, Sipoo, 16. M. Lehtonen, GSF, Espoo, 17. H. Lukkarinen, GSF, Kuopio, 18. T. Manninen, GSF, Rovaniemi, 19. P. Medvedev, Russian Academy of Sciences, Petrozavodsk, 20. D. Mihailova & K. Stepanov, Sevzapgeologija, St. Petersburg, Russia, 21. V. Niiniskorpi, SG Ab, Kiruna, Sweden, 22. J. Paavola, GSF, Kuopio, 23. Y. Pekkala, GSF, Espoo, 24. V. Perttunen, GSF, Rovaniemi, 25. P. Pihlaja, GSF, Espoo, 26. J. Räsänen, GSF, Rovaniemi, 27. P. Rastas, GSF, Rovaniemi, 28. J. Reinikainen, GSF, Espoo, 29. R. Ruotsalainen, National drill core archives, GSF, Loppi, 30. R. Saikkonen, Lohja Oy, Lohja, 31. R. Sarikkola, Outokumpu Oy, Outokumpu, 32. H. Schöberg, Swedish Museum of Natural History, Stockholm, 33. E. Sonninen, University of Helsinki, 34. V. Suominen, GSF, Espoo, 35. E. Tamminen, University of Oulu, 36. M. Torssonen, GSF, Espoo, 37. J. Väänänen, GSF, Rovaniemi, 38. A. Vorma, GSF, Espoo, (GSF = Geological Survey of Finland).

Appendix 1. (continued)

Sample no.	Table no.	Original sample no.	Description	Yield[&]	Grid coordinates x	Grid coordinates y	Source[*]
C-158	1		Medium-grained, light gray marble	10.09	6870.4	4450.2	13
C-160	1	9661	Coarse-grained, white marble	8.05			14
C-161	2	1271/Ramsay	Fine-grained, black dolostone	9.59			14
C-162	2	238/Metzger	Finely crystalline, pink dolostone	9.92			14
C-163	5	42-MSH-78	Fine-grained, gray, tremolite bearing dolostone	7.91	7205.06	3466.89	6
C-164	5	19-MSH-85	Fine-grained, gray, tremolite bearing dolostone	8.49	7185.09	3482.85	6
C-165	2	417/Metzger	Finely crystalline dolostone with stromatolite form *Carelozoon jatulicum (Met.)*	4.29			14
C-168	1		Medium-grained, gray marble	9.27	6895.1	3516.1	13
C-169-A	10	165-1-PJP-80	Banded, white dolostone	8.19	7534.37	3489.48	25
C-170-A	8	R4/3.5m	Finely crystalline, yellowish dolostone, 11 m above the Tikanmaa–Rantamaa formation boundary	9.91	7321.67	2547.95	24
C-170-B	8	R4/5.4m	Finely crystalline, yellowish dolostone, 9 m above the Tikanmaa–Rantamaa formation boundary	9.32	7321.67	2547.95	24
C-170-C	8	R4/8.0m	Finely crystalline, white dolostone, 7 m above the Tikanmaa–Rantamaa formation boundary	9.63	7321.67	2547.95	24
C-170-D	8	R4/10.8m	Finely crystalline, light gray dolostone, 4 m above the Tikanmaa–Rantamaa formation boundary	9.02	7321.67	2547.95	24
C-171-A	8	R7/228.4m	Finely crystalline, pink dolostone	9.10	7322.22	2551.70	24
C-171-C	8	R7/247.8m	Finely crystalline, pink dolostone	9.16	7322.22	2551.70	24
C-171-D	8	R7/249.9m	Finely crystalline, pink dolostone	7.18	7322.22	2551.70	24
C-171-E	8	R7/255.2m	Finely crystalline, pink dolostone	9.29	7322.22	2551.70	24
C-176	5		Medium-grained, pink marble	9.42	7204.05	3449.65	8
C-177-A	4	55-RMA-78	Medium-grained, pink marble, about 100 m below the Petonen–Vaivanen formation boundary	9.35	6971.68	3532.20	17
C-177-B	4	56-RMA-78	Gray marble, transition zone between Petonen and Vaivanen formations	7.16	6971.76	3532.13	17

[&] Total yield of CO_2 as µmol/mg. For pure calcite and dolomite the yields are about 10.0 and 10.8 µmol/mg, respectively.

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Appendix 1. (continued)

Sample no.	Table no.	Original sample no.	Description	Yield[&]	Grid coordinates x	Grid coordinates y	Source[*]
C-179	10	112A-RAR-74	Medium-grained, greenish marble, 10m layer	8.97	7492.08	2509.49	27
C-180	10	62E-ROK-73	Fine-grained, gray marble	7.06	7512.15	2525.06	27
C-181	1		Fine-grained, pure white marble, 10m layer	9.80	6715.3	2535.4	
C-182	1		Fine-grained, white marble, 10m layer	9.19	6714.83	2567.25	
C-187-A	3	R309/64.50m	Medium-grained, pink dolostone	9.64	6924.86	4515.82	29
C-187-B	3	R309/54.50m	Fine-grained, laminated, white dolostone	8.65	6924.86	4515.82	29
C-187-D	3	R309/66.40m	Medium-grained, pink dolostone	10.04	6924.86	4515.82	29
C-188-B	3	R310/174.60	Fine-grained, pink dolostone	8.28	6924.81	4515.68	29
C-188-C	3	R310/164.30	Fine-grained, pink dolostone	10.38	6924.81	4515.68	29
C-188-E	3	R310/135.60	Fine-grained, red calcite rock	9.54	6924.81	4515.68	29
C-188-H	3	R310/82.60	Fine-grained, gray, laminated dolostone	9.85	6924.81	4515.68	29
C-188-J	3	R310/149.70	Fine-grained, pink calcite rock, chert nodules	8.66	6924.81	4515.68	29
C-188-K	3	R310/149.70	Fine-grained, red, laminated calcite-dolomite rock	9.07	6924.81	4515.68	29
C-189-A	3	R311/170.40	Fine-grained, greenish gray, phyllite laminae	7.61	6924.76	4515.54	29
C-189-F	3	R311/123.50	Fine-grained, greenish gray calcite rock	7.24	6924.76	4515.54	29
C-189-J	3	R311/105.40	Fine-grained, gray, tremolite bearing	7.62	6924.76	4515.54	29
C-192-F	4	11-K5-HJL-85	Medium-grained marble, 0.85m from the Petonen–Vaivanen formation boundary	7.86	6980.28	3529.70	17
C-192-G	4	11-K4-HJL-85	1.35m from the Petonen–Vaivanen formation boundary (see C-192-F, C-147)	7.78	6980.28	3529.70	17
C-193-A	8		Finely crystalline, 1m dolostone bed in quartzite	8.59	7312.6	2519.9	24
C-193-B	8		Bottom of a 10m bed in quartzite, 35m higher in stratigraphy compared to C-193-A	9.23	7312.6	2519.9	24
C-193-C	8		Finely crystalline, top of a 10m bed in quartzite	7.85	7312.6	2519.9	24
C-197	8	42-PJM-87	Medium-grained, light gray dolostone	8.74	7385.8	3496.3	3
C-199-A	10		Fine-grained, light gray, laminated dolostone	7.36	7514.0	3443.4	

[&] Total yield of CO_2 as µmol/mg. For pure calcite and dolomite the yields are about 10.0 and 10.8 µmol/mg, respectively.

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Appendix 1. (continued)

Sample no.	Table no.	Original sample no.	Description	Yield[&]	Grid coordinates x	Grid coordinates y	Source[*]
C-200	7		Fine-grained, yellowish marble	10.04	7411.3	4452.3	18
C-201	1		Fine-grained, pure white calcite rock	9.37	6702.00	2482.32	
C-202	1		Medium-grained, white marble	9.21	6670.8	1523.8	34
C-204	1		Medium-grained, light gray marble	8.77	6643.5	1493.9	34
C-205-A	1		Medium-grained, white marble	9.82	6687.6	1529.8	34
C-205-B	1		Fine-grained, white marble	9.67	6687.6	1529.8	34
C-206	1		Medium-grained, white marble	9.66	6724.4	1491.5	34
C-207	1		Fine-graned, gray marble	8.14	6715.3	1505.2	34
C-208-A	109	R6/69,80	Medium-grained, white marble	9.93	7488.45	2478.01	37
C-208-B	10	R6/276,60	Medium-grained, pinkish gray marble	9.30	7488.45	2478.01	37
C-208-C	10	R6/690,10	Medium-grained, gray marble	9.80	7488.45	2478.01	37
C-210-1	7	30	Dolostone, powder sample	7.49	7334.0	4473.7	23
C-210-2	7	55	Dolostone, powder sample	10.03	7364.1	4469.4	23
C-210-4	7	68	Limestone, powder sample	9.70	7365.0	4469.3	23
C-210-5	7	96	Dolostone, powder sample	9.22	7364.0	4480.8	23
C-210-6	7	98	Dolomitic limestone, powder sample	7.58	7364.0	4480.8	23
C-210-7	7	R12/60.0	Dolostone, powder sample	9.95	7365.96	4477.89	23
C-210-8	7	R12/120.0	Dolostone, powder sample	9.43	7365.96	4477.89	23
C-210-10	7	R12/160.0	Dolomitic limestone	8.95	7365.96	4477.89	23
C-211-10	10	SP226/83.00	Finely crystalline, gray dolostone	9.34	7522.5	2517.5	35
C-211-11	10	SP280/72.70	Fine-grained, gray dolostone	8.29	7522.5	2517.5	35
C-212-A	8		Finely crystalline, yellowish dolostone	9.84	7312.62	2521.16	
C-212-B	8		Finely crystalline, gray dolostone, stratigraphic position about 200 m below C-212-A	9.87	7312.58	2520.99	
C-213	8		Finely crystalline, pink dolostone	9.41	7307.6	2541.1	
C-215	10		Finely crystalline, white dolostone	10.07	7513.63	3453.28	16
C-216	10	175F-ROK-75	Medium-grained, gray marble	9.38	7512.15	2506.24	27
C-220-A	10	211-3-LUP-88	Medium-grained, yellowish marble	8.32	7455.3	3503.9	26
C-220-B	10	95-PEM-73	Medium-grained, pink marble, within quartzites	9.43	7454.86	3502.10	26
C-221	10	95-JER-78	Fine-grained, light gray dolostone, within black shales	8.96	7448.00	3546.94	26
C-227-A	10	35-JTV-79	Medium-grained, pink marble	7.83	7478.56	2492.36	37

[&] Total yield of CO_2 as µmol/mg. For pure calcite and dolomite the yields are about 10.0 and 10.8 µmol/mg, respectively.

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Appendix 1. (continued)

Sample	Table	Original	Description	Yield[&]	Grid coordinates		Source[*]
no.	no.	sample no.			x	y	
C-227-B	10	R2/8,3	Medium-grained, gray marble	9.57	7478.56	2492.35	37
C-231-A	5	OKU-796/669.20	Fine-grained, light gray dolomite rock	9.60	6972.60	4466.52	31
C-231-B	5	OKU-796/677.06	Fine-grained, light gray dolomite rock	9.02	6972.60	4466.52	31
C-236-A	10	R39/20.7	Medium-grained, yellowish marble	10.57			21
C-236-B	10	R44/35.0	Medium-grained, white marble	10.59			21
C-237	10	R78062/67	Medium-grained, white marble	10.39			21
C-238	10	TIA-10/45.70	Medium-grained, white marble	9.80			21
C-239	10	R-78096/64.80	Fine-grained, yellowish marble	9.63			21
C-240	10	HUO-27/124,55	Medium-grained, white marble	9.88			21
C-248	6		Finely crystalline, dolostone clast in conglomerate	10.41	7185.96	3561.78	10
C-249-D	7		Finely crystalline, pink dolomite, associated with stromatolites	9.63	7338.75	4469.25	
C-250	10		Finely crystalline, gray limestone	8.94	7508.12	3443.32	
C-252	1		Coarse-grained, white marble, graphite bearing	9.21	6854.42	3517.06	36
C-256	7		Medium-grained, pink marble	10.10	7421.35	4449.35	18
C-257	7		Finely crystalline, pink limestone	9.81	7402.95	4452.75	18
C-262	5		Finely crystalline, dolostone clast in conglomerate	10.63	6999.20	4475.62	9
C-263	3	11-Höy-89	Fine-grained, light gray dolostone	9.58	7004.6	4457.11	10
C-266	5		Fine-grained, dark gray dolostone, 0.9m bed within black shales	9.67	7102.88	3552.10	5
C-271	4		Fine-grained, pinkish dolostone	9.97	7012.88	3568.68	22
C-273	1		Medium-grained, white marble	10.14	6912.32	3522.56	28
C-277-1	7	R12/107.5	Finely crystalline, yellowish white dolostone	9.44	7365.96	4477.89	29
C-277-2	7	R12/136.5	Finely crystalline, white dolostone	10.09	7365.96	4477.89	29
C-280	6	132-1A-AVL-89	Finely crystalline, pinkish dolostone	9.91	7151.96	3527.74	10
C-281-1	8		Fine-grained, white marble	9.30	7385.8	3496.3	
C-281-2	8		Fine-grained, white marble	9.94	7385.8	3496.3	
C-281-3	8		Fine-grained, light gray marble	8.75	7385.8	3496.3	
C-281-4	8		Fine-grained, white marble	9.37	7385.8	3496.3	
C-282-1	10	R375/56.80	Finely crystalline, white dolostone	10.13	7518.30	2540.70	29

[&] Total yield of CO_2 as µmol/mg. For pure calcite and dolomite the yields are about 10.0 and 10.8 µmol/mg, respectively.

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Appendix 1. (continued)

Sample no.	Table no.	Original sample no.	Description	Yield[&]	Grid coordinates x	Grid coordinates y	Source[*]
C-282-3	10	R375/51.00	Finely crystalline, light gray dolostone	10.20	7518.30	2540.70	29
C-283-1	6	R356/3,30	Fine-grained, white dolostone	8.30	7185.45	3537.09	29
C-283-2	6	R353/41,30	Fine-grained, light gray dolostone	9.09	7184.40	3536.46	29
C-283-3	6	R356/13.50	Fine-grained, light gray calcitic dolostone	8.24	7185.45	3537.09	29
C-283-4	6	R353/29.50	Fine-grained, light gray dolostone	10.01	7184.40	3536.46	29
C-284	6		Fine-grained, white dolostone	10.06	7166.96	3543.69	10
C-287-A	2		Finely crystalline, pink dolostone from bed containing stromatolites of the *Sundosia* group	9.21			38
C-287-B	2		Finely crystalline, in stratigraphy ca. 17m below C-287-A. Bed with *Nuclephyton* stromatolites	10.25			38
C-290	1		Medium-grained, white marble	9.30	6773.70	2430.32	
C-291	4		Medium-grained, light gray marble	9.78	6956.76	3541.28	1
C-292-1	1	R378/216,85	Medium-grained, light gray marble	8.96	6871.80	3530.27	1
C-292-4	1	R377/131,1	Medium-grained, light gray marble	8.29	6871.32	3530.67	1
C-293-2	1	R303/52,5	Medium-grained, light gray marble	7.70	7036.28	3477.33	1
C-293-3	1	R303/61,1	Medium-grained, light gray marble	7.86	7036.28	3477.33	1
C-297	1		Coarse-grained, light gray marble inclusion in ultramafic pillow lava	9.21	6683.13	2470.09	
C-298-A	8		Medium-grained, white marble	10.53	7361.30	3492.18	3
C-303	6		Finely crystalline, white calcitic dolostone	9.80	7172.92	3544.58	10
C-304	6		Medium-crystalline, white dolostone	10.14	7144.94	3536.20	10
C-305-1	10	R3/97.85	Fine-grained, yellowish white dolostone	10.34	7509.50	3469.94	26
C-305-2	10	R3/65.50	Fine-grained, white limestone, tremolite bearing	9.37	7509.50	3469.94	26
C-305-3	10	R3/25.70	Fine-grained, light gray dolostone	10.12	7509.50	3469.94	26
C-315-A	10		Finely crystalline, white siliceous dolostone	6.36	7494.20	3459.40	
C-315-B	10		Finely crystalline, white siliceous dolostone	6.96	7494.20	3459.40	
C-315-C	10		Finely crystalline, laminated siliceous dolostone	6.33	7494.20	3459.40	
C-315-D	10		Finely crystalline, laminated siliceous dolostone	6.30	7494.20	3459.40	
C-316	1		Medium-grained, light gray marble	8.53			

[&] Total yield of CO_2 as µmol/mg. For pure calcite and dolomite the yields are about 10.0 and 10.8 µmol/mg, respectively.

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Appendix 1. (continued)

Sample no.	Table no.	Original sample no.	Description	Yield[&]	Grid coordinates x	y	Source[*]
C-317-A	9		Finely crystalline, gray dolostone with stromatolite structures, 0.6m carbonate bed	8.13			
C-317-B	9		Same as C-317-A, 0.2m carbonate bed	7.28			
C-323-A	7		Fine-grained, light gray dolostone	10.66	7352.68	4470.60	
C-323-B	7		Fine-grained, white dolostone	9.87	7352.68	4470.60	
C-323-C	7		Fine-grained, pink dolostone	10.22	7352.68	4470.60	
C-324	7		Fine-grained, pinkish dolostone	10.40	7364.15	4469.70	
C-327	7	10.3-TEM-91	Finely crystalline pink dolostone	10.33	7371.11	4467.31	18
C-328-1	2	10/4n	Fine-grained dolostone, ca. 400m below the Ludian–Jatulian boundary	9.72			20
C-328-2	2	9/4n	Fine-grained dolostone, ca. 400m below the Ludian–Jatulian boundary	9.06			20
C-328-3	2	C28/136.5m	Fine-grained, pink dolostone, ca. 76m below the Ludian–Jatulian boundary	9.77			20
C-328-4	2	C28/101.0m	Fine-grained, hematite bearing dolostone, ca. 40 m below the Ludian–Jatulian boundary	10.41			20
C-328-5	2	C28/96.0m	Fine-grained, pink dolostone, ca. 35m below the Ludian–Jatulian boundary	9.89			20
C-328-6	2	C39/18.5m	Fine-grained, light gray dolostone, about 200 m above the Ludian–Jatulian boundary	8.94			20
C-330-A	4		Medium-grained, white marble	8.59			
C-330-B	4		Medium-grained, white marble	8.88			
C-331-A	4		Fine-grained, white marble	9.91			
C-331-B	4		Fine-grained, light gray marble	9.20			
C-332-A	4		Medium-grained, white marble	9.51			
C-332-B	4		Fine-grained, white marble	9.43			
C-333	4		Fine-grained, white marble	7.70			
C-334-A	4		Medium-grained, white marble	9.35			
C-334-B	4		Medium-grained, white marble	9.59			
C-346	7		Finely crystalline, light gray dolostone	7.09			27
C-347-B	10	30c-MON-76	Fine-grained, pink dolostone, laminated	8.56	7439.2	3505.8	26
C-348-A	10	21-JAK-74	Medium-grained, light gray marble	9.28	7443.42	3503.52	26

[&] Total yield of CO_2 as µmol/mg. For pure calcite and dolomite the yields are about 10.0 and 10.8 µmol/mg, respectively.

[*] Source of samples: 1. E. Ekdahl, GSF, Kuopio, 2. J. Hallikainen, Lapin Marmori Oy, Loue, 3. E. Hanski, GSF, Rovaniemi, 4. R. Harinen, Partek Minerals Oy, Parainen, 5. M. Havola, GSF, Kuopio, 6. M. Honkamo, GSF, Rovaniemi, 7. P. Karhunen, Mineralogical Museum, GSF, Espoo, 8. R. Kesola, GSF, Kuopio, 9. J. Kohonen, GSF, Espoo, 10. A. Kontinen, GSF, Kuopio, 11. J. Kurki, Outokumpu Oy, Outokumpu, 12. I. Lager, Luleå University, Sweden, 13. M. Lehtinen, Partek Minerals Oy, Lappeenranta, 14. M. Lehtinen, Geological Museum, University of Helsinki, 15. P. Lehtinen, Lohja Oy, Sipoo. 16. M. Lehtonen, GSF, Espoo, 17. H. Lukkarinen, GSF, Kuopio, 18. T. Manninen, GSF, Rovaniemi, 19. P. Medvedev, Russian Academy of Sciences, Petrozavodsk, 20. D. Mihailova & K. Stepanov, Sevzapgeologija, St. Petersburg, Russia, 21. V. Niiniskorpi, SG Ab, Kiruna, Sweden, 22. J. Paavola, GSF, Kuopio, 23. Y. Pekkala, GSF, Espoo, 24. V. Perttunen, GSF, Rovaniemi, 25. P. Pihlaja, GSF, Espoo, 26. J. Räsänen, GSF, Rovaniemi, 27. P. Rastas, GSF, Rovaniemi, 28. J. Reinikainen, GSF, Espoo, 29. R. Ruotsalainen, National drill core archives, GSF, Loppi, 30. R. Saikkonen, Lohja Oy, Lohja, 31. R. Sarikkola, Outokumpu Oy, Outokumpu, 32. H. Schöberg, Swedish Museum of Natural History, Stockholm, 33. E. Sonninen, University of Helsinki, 34. V. Suominen, GSF, Espoo, 35. E. Tamminen, University of Oulu, 36. M. Torssonen, GSF, Espoo, 37. J. Väänänen, GSF, Rovaniemi, 38. A. Vorma, GSF, Espoo, (GSF = Geological Survey of Finland).

Appendix 1. (continued)

Sample no.	Table no.	Original sample no.	Description	Yield[&]	Grid coordinates x	Grid coordinates y	Source[*]
C-348-B	10	22c-JAK-74	Medium-grained, yellowish marble with euhedral, brown albite crystals	8.67	7443.46	3503.58	26
C-349-A	2		Finely crystalline dolostone, with stromatolite form *Stratifera ordinata (Mak.)*	8.85			19
C-349-B	2		Same sample as C-349-A, stromatolite form *Butinella boreale (Mak.)*	9.98			19
C-350	2		Finely crystalline dolostone with stromatolite form *Sundozia miza (But.)*	8.66			19
C-351	2		Finely crystalline dolostone with stromatolite form *Segosia columnaris (But.)*	9.25			19
C-352-A	8	R23/246.0m	Finely crystalline, light gray dolostone	7.51	7346.13	2527.49	24
C-359	10	60-PPN-79	Medium-grained, yellowish marble	8.26	7441.10	3543.29	26
C-366	1	R22/37,20	Coarse-grained, white marble	9.39	6883.6	3529.2	28
C-369	9		Finely crystalline, gray calcitic dolostone	7.64			32
C-370-1	9	Kal501	Finely crystalline, white dolostone	10.23			12
C-370-2	9	Kal908	Finely crystalline, white dolostone	9.35			12
C-370-3	9	Kal925	Finely crystalline, laminated, white dolostone	9.83			12
C-370-4	9	Kal927	Finely crystalline, laminated, gray dolostone	7.61			12
C-371	2	1260/Ramsay	Finely crystalline, white dolostone	10.41			14
C-372	2	241/Eskola	Fine-grained, light gray limestone	9.00			14

[&] Total yield of CO_2 as μmol/mg. For pure calcite and dolomite the yields are about 10.0 and 10.8 μmol/mg, respectively.

[*] Source of samples: 1. E. Ekdahl, GSF, Kuopio, 2. J. Hallikainen, Lapin Marmori Oy, Loue, 3. E. Hanski, GSF, Rovaniemi, 4. R. Harinen, Partek Minerals Oy, Parainen, 5. M. Havola, GSF, Kuopio, 6. M. Honkamo, GSF, Rovaniemi, 7. P. Karhunen, Mineralogical Museum, GSF, Espoo, 8. R. Kesola, GSF, Kuopio, 9. J. Kohonen, GSF, Espoo, 10. A. Kontinen, GSF, Kuopio, 11. J. Kurki, Outokumpu Oy, Outokumpu, 12. I. Lager, Luleå University, Sweden, 13. M. Lehtinen, Partek Minerals Oy, Lappeenranta, 14. M. Lehtinen, Geological Museum, University of Helsinki, 15. P. Lehtinen, Lohja Oy, Sipoo, 16. M. Lehtonen, GSF, Espoo, 17. H. Lukkarinen, GSF, Kuopio, 18. T. Manninen, GSF, Rovaniemi, 19. P. Medvedev, Russian Academy of Sciences, Petrozavodsk, 20. D. Mihailova & K. Stepanov, Sevzapgeologija, St. Petersburg, Russia, 21. V. Niiniskorpi, SG Ab, Kiruna, Sweden, 22. J. Paavola, GSF, Kuopio, 23. Y. Pekkala, GSF, Espoo, 24. V. Perttunen, GSF, Rovaniemi, 25. P. Pihlaja, GSF, Espoo, 26. J. Räsänen, GSF, Rovaniemi, 27. P. Rastas, GSF, Rovaniemi, 28. J. Reinikainen, GSF, Espoo, 29. R. Ruotsalainen, National drill core archives, GSF, Loppi, 30. R. Saikkonen, Lohja Oy, Lohja, 31. R. Sarikkola, Outokumpu Oy, Outokumpu, 32. H. Schöberg, Swedish Museum of Natural History, Stockholm, 33. E. Sonninen, University of Helsinki, 34. V. Suominen, GSF, Espoo, 35. E. Tamminen, University of Oulu, 36. M. Torssonen, GSF, Espoo, 37. J. Väänänen, GSF, Rovaniemi, 38. A. Vorma, GSF, Espoo, (GSF = Geological Survey of Finland).

Appendix 2. Descriptions and locations of black shale samples.

Sample no.	Original sample no.	Description	Grid coordinates x	y	Source*)
K-1	13-HJL-85	Old graphite quarry at Laivonsaari, Kuopio	6980.68	3529.66	6
K-9-A	R311/187.1	Graphitic schist, drill core sample	6924.76	4515.54	5
K-9-B	R315/45.8	Graphitic schist, drill core sample	6924.76	4515.54	5
K-9-C	R430/50.0	Graphitic schist, drill core sample	6925.43	4515.44	10
K-9-D	R430/57.0	Graphitic schist, drill core sample	6925.43	4515.44	10
K-10-A	Ju/Pe 9/100.2	Graphitic schist, drill core sample	7001.48	4453.42	5
K-10-B	JuPe12/135.9	Graphitic schist, drill core sample	7001.27	4456.76	5
K-10-C	R302/22.0	Graphitic schist, drill core sample	7007.44	4456.81	10
K-10-D	R303/27.5	Graphitic schist, drill core sample	7007.24	4456.82	10
K-10-E		Graphitic schist	7009.0	4456.0	4
K-25		Shungite, very high contents of C, Lake Onega area			3
K-32	52-PM/KS-61	Black shale, concretion bearing, "Calu precambricus"	7352	4469	1
K-60	R6/182.6	Sulfide bearing black shale, drill core sample	7470.77	3552.87	2
K-63-1	104-PJP-80	Black shale, below Sattasvaara Formation	7520.80	3490.81	7
K-63-2	77-KOS-80	Black shale, below Sattasvaara Formation	7524.13	3491.61	7
K-63-3	76-RAN-82	Black shale, below Sattasvaara Formation	7520.91	3482.17	7
K-63-4	62-1-TEM-83	Black shale, below Sattasvaara Formation	7532.90	3496.22	7
K-65	R15/217.90	Sulfide bearing black shale, drill core sample	7512.76	2561.99	9
K-100		Black shale intercalations in tuffite	7346.40	4462.87	
K-112-1	R3/10.4	Black shale, thin pyroclastic intercalations	7509.50	3469.94	8
K-112-2	R3/13.0	Laminated black shale	7509.50	3469.94	8
K-112-3	R3/23.6	Laminated black shale, thin pyroclastic intercalations	7509.50	3469.94	8
K-112-4	R3/32.9	Black shale, as intercalations in ultramafic tuffite	7509.50	3469.94	8
K-112-5	R3/45.7	Black shale, thin pyroclastic intercalations	7509.50	3469.94	8
K-112-6	R3/11.5	Black shale bed in gray phyllite	7509.50	3469.94	8
K-112-7	R3/55.7	Black shale, pyroclastic intercalations	7509.50	3469.94	8
K-112-8	R3/42.7	Black shale interlayer in ultramafic tuffite	7509.50	3469.94	8
K-112-9	R3/61.2	Black shale interlayer in ultramafic tuffite	7509.50	3469.94	8

*) Source of samples: 1. M. Huhma, Espoo, 2. H. Juopperi, GSF, Rovaniemi, 3. P. Karhunen, Mineralogical Museum, GSF, Espoo, 4. A. Kontinen, GSF, Kuopio, 5. K. Loukola-Ruskeeniemi, GSF, Espoo, 6. H. Lukkarinen, GSF, Kuopio, 7. P: Pihlaja, GSF, Espoo, 8. J. Räsänen, GSF, Rovaniemi, 9. P. Rastas, GSF, Rovaniemi, 10. O. Sarapää, GSF, Espoo, (GSF= Geological Survey of Finland).

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