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*Frau Prof. Dr. Emilie Jäger gewidmet*

## Rb–Sr and oxygen isotope geochemistry on a complex Proterozoic intrusive, Vaaraslahti, Finland

by *Ueli Haudenschild<sup>1</sup>* and *Bruno J. Giletti<sup>2</sup>*

### Abstract

Plagioclase – K-feldspar – whole-rock Rb–Sr isochrons yield ages of  $1809 \pm 4$  and  $1814 \pm 12$  Ma for a monzonitic and a granitic sample of the same mangerite intrusion. Biotite separated from the granitic sample yielded a Rb–Sr age of  $1750 \pm 18$  Ma. The Rb–Sr system of the 1884 Ma old intrusion therefore must have been reequilibrated after emplacement. Owing the feldspar data the reset of the strontium system may be attributed to a second thermal event at 1810 Ma exceeding the closure temperature (500–550 °C) of the feldspars. A slow cooling rate at low temperatures allowing low temperature volume diffusional strontium exchange may explain the difference between the Rb–Sr (1750 Ma) and the K–Ar (1781 Ma) biotite ages, the closure temperature for strontium diffusion being somewhat lower than the 300 °C blocking temperature used for the K–Ar system. (The terms "closure" and "blocking" temperature were used to distinguish between the temperature calculated for oxygen and strontium using the formula of DODSON [1973] and the empirical temperatures of 300 °C [biotite] and 550 °C [hornblende] related to the apparent radiometric K–Ar ages.)

Oxygen isotope analyses were made on pyroxene, hornblende, biotite, quartz, plagioclase, K-feldspar, magnetite, garnet, and whole-rock concentrates of the same samples yielding mostly "normal" granitic values. The influence of meteoric water on the cooling system therefore can be excluded, e.g. the fluids controlling the strontium exchange can be assumed as coming out of the intrusive body or underlaying units with similar  $\delta^{18}\text{O}$  characteristics.

Using the oxygen data for cooling rate calculations pyroxene, hornblende and quartz results indicate a cooling rate in the order of 30 °C/Ma (with an uncertainty of a factor of 3) for the high temperature portion of the cooling process, which is in agreement with the radiogenic isotope data for the early stages of cooling.

**Keywords:** Rb–Sr, oxygen isotopes, cooling rate, closure temperature, diffusion, Proterozoic, Finland.

### 1. Introduction

Strontium isotopes have a wide application to problems of petrogenesis and age determination. Rb–Sr whole-rock isochrons may yield the crystallization-age of plutonic rocks while mineral data often reflect the time of metamorphism or cooling (FAURE 1986; JÄGER, 1979). Oxygen isotope data provide information on the magma genesis (PANKHURST et al., 1976; HILL et al., 1986), the metamorphic (HUEBNER et al., 1986; JIANG et al., 1988) and the cooling history (GILETTI, 1986) or the extent of meteoric water–rock interactions (FORESTER and TAYLOR, 1977).

This paper presents strontium and oxygen isotopic data on the synkinematic mangerite intrusion at Vaaraslahti situated within the proterozoic Svecokarelian belt of Eastern Finland. Isotope studies

were used to investigate material exchange processes during the cooling of the plutonic body. A model for the petrogenesis and cooling of the Vaaraslahti intrusive will be presented, which derives from stable and radiogenic isotope data. Similar investigations on the metasedimentary host-rock of this intrusion are in preparation.

### 2. Geology

The Vaaraslahti mangerite intrusion lies in eastern Finland, about 15 km north of the village of Pielassesi (Fig. 1). It is situated within the NW–SE trending "Raahe-Ladoga zone" (MARTTILA, 1976) also called the main sulphide ore belt (NEUVONEN et al., 1981) thought to represent the suture zone between the Proterozoic Svecokarelian orogen in

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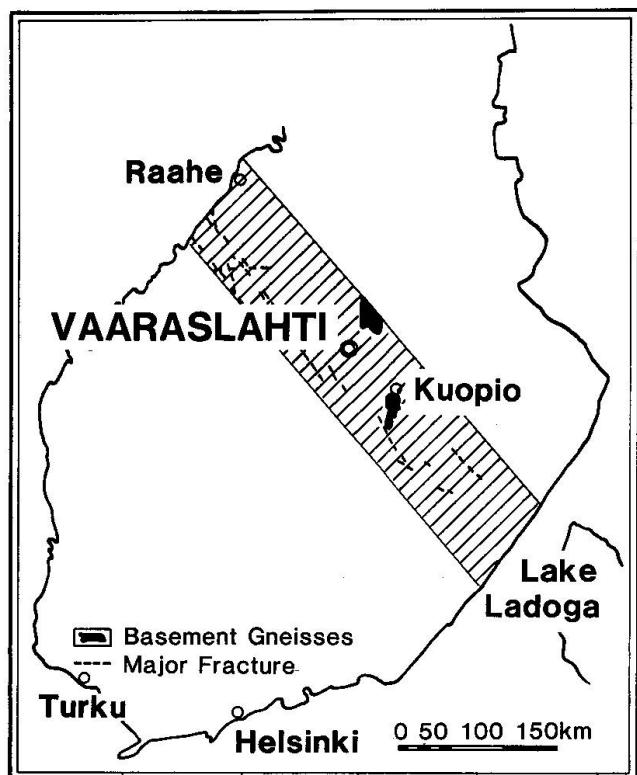


Fig. 1 Sketchmap of Southern Finland showing the location of Vaaraslahti within the main sulphide ore-belt running from northwest to southeast between Raahen and Lake Ladoga (after NEUVONEN et al., 1981).

the southwest and the Archean craton in the northeast (KORSMAN, 1988).

The intrusion is part of the next to the last (from west to east) of a succession of seven tectonometamorphic blocks (Lampaanjärvi block) bordering the Archean basement gneisses in the east. It is rectangular to elliptic in shape with its largest diameter of 3.5 km aligned NE-SW. It mainly consists of pyroxene-granite, some quartz-syenitic to monzonitic components up to 0.5 km in diameter grading into the granite. The major mineral components of the granitic variety are K-feldspar (44%), plagioclase (24.5%), quartz (24%), and biotite (7.5%), with occasional garnet, hornblende and hypersthene. The monzonitic variety contains K-feldspar, plagioclase, quartz, biotite, hornblende, hypersthene, magnetite and diopside. The grain sizes are approximately 0.5–1 mm (mafics) and 1–5 mm (quartz, plagioclase). Porphyritic K-feldspars can be up to 1 cm long. The modes and grain sizes are given in table 2. In the outcrop the intrusion has a plutonic texture with no preferred orientation. Mineral reactions such as between hornblende and biotite and myrmecitic quartz in feldspar were observed in thin section.

The host-rocks of the intrusion are mainly metapelites intercalated with mafic metavolcanites

(amphibolites). The metamorphic conditions were described by HÖLTTÄ (1988). In a 100–200 m wide contact aureole around the intrusion the grade of metamorphism increases from amphibolite to granulite facies (HÖLTTÄ et al., in prep.). Metamorphic temperatures around 600–650 °C were calculated using various paleothermometers (HÖLTTÄ, 1988) increasing up to 750–800 °C close to the contact with the mangerite. Corresponding pressures were estimated at 4.5–5.5 kb (HÖLTTÄ op. cit.). Retrograde reactions, also found within the area of contact metamorphic influence, affected the whole block and postdate the intrusion (HÖLTTÄ op. cit.). Decomposition of sillimanite and cordierite to biotite and muscovite even in potassium deficient rocks were explained by HÖLTTÄ (1988) as implying that the K-feldspar was totally consumed or that the reaction occurred under the influence of a potassium bearing fluid. Metamorphic conditions of lower amphibolite facies were found in blocks (Pihtipudas) west of the Pielavesi block.

The intrusion was dated by U-Pb zircon analyses at  $1885 \pm 5$  Ma (SALLI, 1983), a monazite U-Pb age was only slightly younger (1874 Ma). Whole-rock Rb-Sr analysis of the host-rock yielded an isochron age of  $1889 \pm 8$  Ma (HÖLTTÄ et al., in prep.). Comparable ages were measured on monazites and zircons of the metapelite taken at the immediate contact to the intrusion while zircons taken at a distance of only 80 m to the contact revealed ages in excess of 2000 Ma (VAASJOKI and SAKKO, 1988). K-Ar biotite ages near the contact vary between 1770–1790 Ma. Cooling ages of 1740 Ma (Rb-Sr on muscovite), 1650 Ma (K-Ar on muscovite) and 1620 Ma (K-Ar on biotite) were measured in the eastern part of the Lampaanjärvi block (HAUDENSCHILD, 1988, 1990).

### 3. Analytical procedure

Fresh samples of about 5 kg each were taken one by blasting, one by hand along a roadcut. The rocks were crushed in a stainless steel mortar to a grain-size less than 5 mm and sieved to grain-size fractions of > 2 mm, 1–2 mm, 0.7–1 mm, 0.5–0.7 mm, 0.35–0.5 mm, 0.125–0.35 mm and less than 0.125 mm. K-feldspar grains larger than 5 mm were cut out of the hand specimen using a dentist-drill, crushed and hand picked. Whole-rock samples were prepared by splitting the crushed sample to a volume of 200 ml. Mineral concentrates were obtained by magnetic and heavy-liquid separation and subsequent hand-picking.

Rb and Sr analyses were performed at the Department for Isotope Geology of the University of Bern. The samples were dissolved in a perchloric-

hydrofluoric acid mixture and spiked with highly concentrated  $^{84}\text{Sr}$  and  $^{87}\text{Rb}$  tracer. Rb and Sr were separated on ion-exchange columns. Rb was analysed on a solid source single collector mass spectrometer made by Ion Equipments with 35 cm radius and a three-filament ion source. Sr was measured on a VG-Sector mass-spectrometer with 26 cm radius, five collectors and a single-filament ion source. The ages were calculated using the IUGS recommended constants (STEIGER and JÄGER, 1977).

Oxygen isotope analyses were done at the Department of Geological Sciences of Brown University, Providence, R.I., using the technique described by CLAYTON and MAYEDA (1963). Samples of 5 to 10 mg were placed in nickel vessels, which were flooded with nitrogen gas during the loading procedure to minimize contamination of the vessels with air oxygen and water-vapour. After loading the vessels were pumped for two hours. Aliquots of  $\text{BrF}_5$  at about twice the stoichiometric reaction amount were frozen into each vessel using liquid nitrogen. The vessels were thawed to room temperature to allow the  $\text{BrF}_5$  to react with any air oxygen/water adsorbed on the sample surface. The  $\text{BrF}_5$  was frozen in the vessels again and the vessels evacuated to remove oxygen released during this pretreatment.

The samples were reacted with the  $\text{BrF}_5$  at 600 °C (650 °C for garnet and magnetite) for twelve hours. The oxygen extracted was converted to  $\text{CO}_2$  by reaction with a hot carbon rod. Sample yields were measured in a calibrated volume. The  $\text{CO}_2$  was analyzed in a VG Isogas mass-spectrometer. The results are expressed in standard notation relative to standard mean ocean water (SMOW). The value and reproducibility of the ARK quartz-standard run simultaneously with each set of samples was  $+18.37 \pm 0.18\text{‰}$  (1  $\sigma$ ) (see results below) while the 1  $\sigma$  analytical error of the mineral and whole-rock measurements was  $\pm 0.27\text{‰}$ . Concurrent analyses of NBS-28 quartz standard gave  $+9.8 \pm 0.2\text{‰}$ .

The mineral mode of the samples was determined by point-counting. K-feldspar, plagioclase, quartz and biotite abundances were counted by the use of a grid laid over the stained surface of sample slabs. 606 points were counted on the granitic sample, 778 points on the monzonite. The mafic minerals of the monzonite had to be counted together. The relative abundances of amphibole, pyroxene, biotite and magnetite were determined in thin section. The volume percentages were used to determine the oxygen mol-% contribution of each mineral to the whole-rock.

Grain sizes were measured in thin section. For quartz, plagioclase, magnetite, and the biotite of

the granitic sample, the grain-sizes used for the analyses exceeded the measured ones, e.g. the separated mineral grains consist of more than one specimen each. This implies that more or less the whole grain from rim to core was actually present in the analysed mineral separate. Pyroxene, and especially hornblende and biotite of the monzonite were strongly intergrown and had to be separated out of a sieve fraction about half of the size of the measured grain-sizes. K-feldspars were separated as whole grains directly out of the rock. The analysed material therefore may also represent the whole crystal, also perthitic exsolution may indicate that the effective distance for diffusion from grain-boundary to grain-boundary might correspond to the width of the lamellae, e.g. being much smaller than the size of the grains. As shown by DODSON (1986) changing isotope fractionation factors with decreasing temperature result in an isotope composition gradient across the mineral grain, with the largest gradient near the rim, and the smallest in the core. Due to the loss of mainly rim material during mineral separation, the calculated cooling rates for pyroxene, hornblende and biotite may represent a maximum.

## 4. Results

### 4.1. RUBIDIUM-STRONTIUM

The analytical results for the biotite, feldspar and whole-rock analyses are given in table 1.

Plagioclase, K-feldspar and whole-rock define isochrons of  $1814 \pm 12$  Ma and  $1809 \pm 4$  Ma (Fig. 2a) for the granitic and the monzonitic samples respectively (the uncertainty in the isochron age is determined from the standard deviation of the regression line). The samples essentially define two-point isochrons owing the close similarity of the Rb-Sr K-feldspar and whole-rock data of the granitic rock and the whole-rock consisting up to 93% of feldspars (as the main Rb-Sr bearing phases) and quartz (non Rb-Sr bearing phase), the Rb/Sr ratio of the whole-rock representing a mixture between the two feldspar values. The isochron ages may be explained as to be caused by diffusive low temperature strontium reequilibration or by a postmagmatic disturbance of the Rb-Sr system.

The biotite of the granitic sample corrected with its whole-rock value, has an age of  $1750 \pm 18$  Ma which is substantially lower than the K-Ar age (1780 Ma) of the same sample (HÖLTTÄ et al., in prep) and the K-Ar biotite ages of 1760–1790 Ma (HAUDENSCHILD, 1988) measured in the immediate vicinity.

Tab. 1 Rb-Sr analytical data for the Vaaraslahti mangerite.

Sample	Mineral	Rb total (ppm)	Sr total (ppm)	$87\text{Rb}/86\text{Sr}$	$87\text{Sr}/86\text{Sr}$	% Std Dev
KAW 3328	whole-rock	156.75	115.07	3.980125	0.808508	0.0014
KAW 3328	microcline	261.53	187.20	4.082683	0.810409	0.0026
KAW 3328	plagioclase	14.40	207.06	0.201252	0.709483	0.0016
KAW 3328	biotite	745.65	7.60	942.984820	24.440748	0.0107
KAW 3329	whole-rock	119.59	159.92	2.174938	0.761320	0.0015
KAW 3329	microcline	217.08	195.89	3.231601	0.788660	0.0019
KAW 3329	plagioclase	8.03	227.19	0.102320	0.707272	0.0057

## 4.2. OXYGEN

The analytical results for mineral and whole-rock measurements are given in table 2. The internal ARK quartz-standard, analysed 14 times simultaneously with the samples gave a mean value for

$\delta^{18}\text{O}$  of  $18.37 \pm 0.18\text{‰}$ . PDQ quartz-standard was analysed as  $7.19 \pm 0.20\text{‰}$ .

The whole-rock  $\delta^{18}\text{O}$  values of  $9.99\text{‰}$  and  $9.66\text{‰}$  for the granitic and the monzonitic samples respectively, both lie within the range of "normal" ( $+7$  to  $+10\text{‰}$   $\delta^{18}\text{O}$  relative to SMOW) granitic

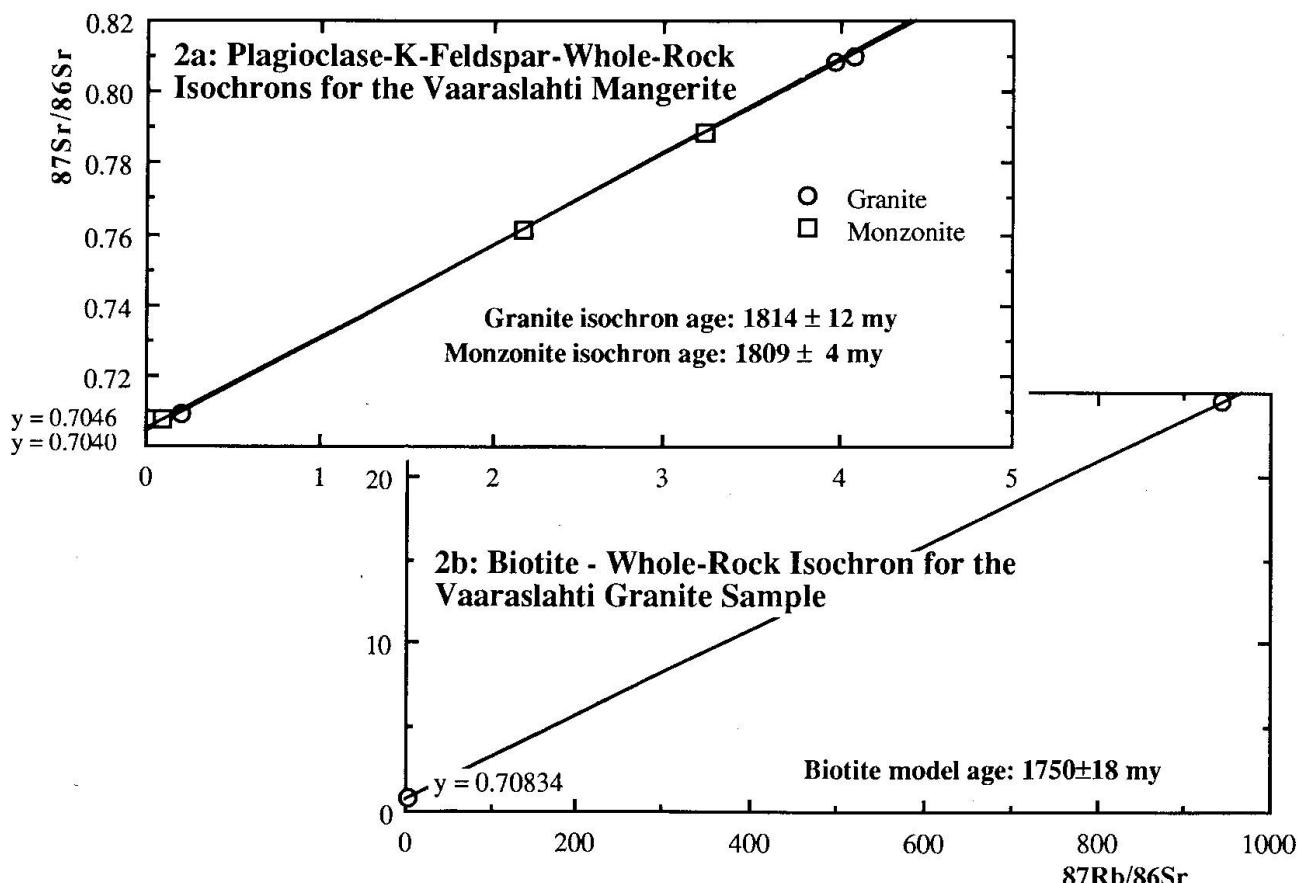


Fig. 2 a) Plagioclase-K-feldspar-whole-rock isochrons for the Vaaraslahti mangerite showing isochron ages and initial  $^{87}\text{Sr}/^{86}\text{Sr}$  values for both samples. The y-values of 0.7046 and 0.7040 correspond to the monzonitic and the granitic samples respectively.

b) Biotite-whole-rock isochron for the granitic sample of the Vaaraslahti mangerite.

Tab. 2 Analytical results of the Vaaraslahti samples used for the oxygen cooling rate calculations.

Sample	Mineral	Mode %	Grain radius (cm)	$\delta^{18}\text{O}$ (SMOW)
KAW 3328	quartz	26.78	0.175	11.48
KAW 3328	microcline	40.95	0.250	9.42
KAW 3328	plagioclase	24.54	0.150	9.24
KAW 3328	biotite	7.10	0.075	7.28
KAW 3328	garnet	0.63	0.035	7.88
KAW 3328	whole rock			9.99
KAW 3329	quartz	11.39	0.175	11.31
KAW 3329	microcline	45.99	0.250	9.44
KAW 3329	plagioclase	35.55	0.150	9.19
KAW 3329	biotite	1.79	0.050	7.11
KAW 3329	hornblende	1.78	0.100	7.95
KAW 3329	pyroxene	2.85	0.075	8.27
KAW 3329	magnetite	0.65	0.015	4.97
KAW 3329	whole rock			9.66

rocks (FAURE, 1986). The mineral analyses also show normal plutonic  $\delta^{18}\text{O}$  characteristics with quartz being the heaviest and magnetite being the lightest. No minerals show any hydrothermal influence of meteoric water which should lower the  $\delta^{18}\text{O}$  values of biotite and feldspars even at temperatures as low as 300–400 °C.

#### 4.3. MODELLED COOLING RATES

For an optimal visualization of the oxygen data cooling rates for both rock samples were calculated using the model of GILETTI (1986). This is a forward calculation where a cooling rate is assumed, measured mineral particle sizes are used to compute closure temperatures for each mineral (DODSON, 1973), and the highest closure temperature is the starting point for the calculation. Oxygen isotope equilibrium is assumed at that temperature, and the mode of the rock, plus the whole rock  $\delta^{18}\text{O}$ , are used to compute the  $\delta^{18}\text{O}$  values of the minerals.

Fractionation factors were taken from BOTTINGA and JAVOY (1975), except for biotite, where the temperature dependent term, B, was taken to be  $1.5 \times 10^6$  (BERTENRATH and FRIEDRICHSEN, 1975). The first minerals to close are clinopyroxene and garnet. The process is repeated until all minerals are closed. The computation is then repeated for other cooling rates. The crux of the model is that different cooling rates result in different closure temperatures, and since the different temperatures imply different fractionation factors for oxygen isotopes, the minerals should have different  $\delta^{18}\text{O}$  values depending on the cooling and the mineral modes.

A graph can be constructed showing the different  $\delta^{18}\text{O}$  values as a function of cooling rate (Fig. 3a, 3b). The measured mineral  $\delta^{18}\text{O}$  values are shown as horizontal lines. If the cooling rock remained a closed system, the intersection of the model minerals with their respective measured values should give the cooling rate. If the rock cooled at a constant rate, all intersections should occur at the same cooling rate.

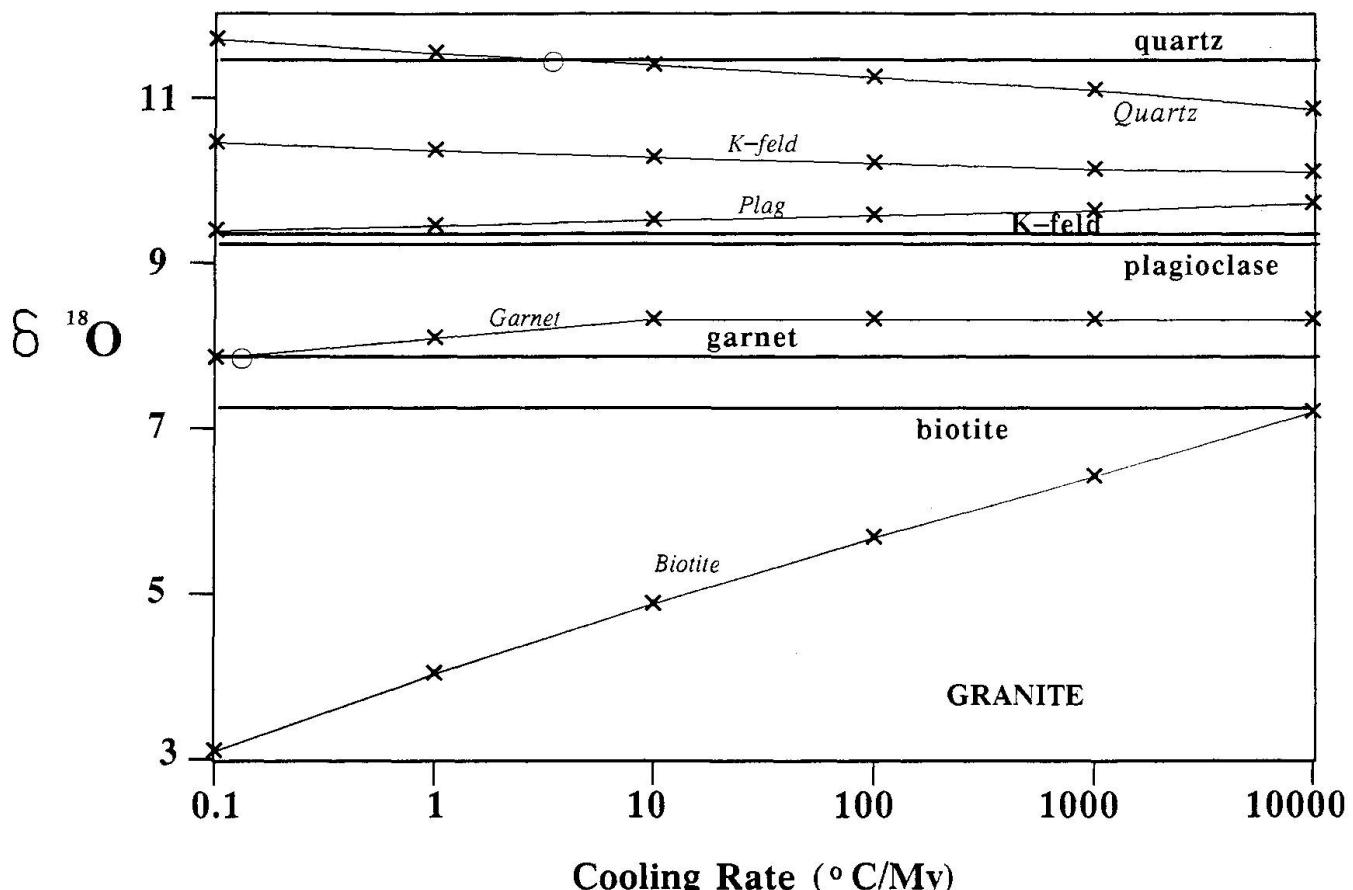


Fig. 3a Graph of the cooling rate calculations for the granite sample giving the measured (bold lines) and the calculated (thin lines)  $\delta^{18}\text{O}$  values and the corresponding cooling rates (open circles).

It will be noted that the model lines for clino-pyroxene, hornblende, and garnet become flat at the high cooling rates. This is because the closure temperatures for these minerals are higher than the solidus of the monzonite and granite, respectively, where cooling is rapid. Consequently, these minerals crystallized as closed systems in those cases, and reflect equilibrium at the solidus temperature.

Neither rock gives a consistent set of cooling rates. Given the uncertainties in the model, a scatter of a factor of four in cooling rate can be expected (FORTIER, 1990). Note that the most abundant minerals, the feldspars, will "buffer" the rock. They have a  $\delta^{18}\text{O}$  value that does not change much with cooling rate. The other minerals will change with respect to the feldspars. Consequently, intersections of the almost-parallel lines (horizontal data lines vs. almost horizontal model feldspar lines) have little significance.

In the case of the monzonite, the quartz, pyroxene, and hornblende all have moderate slopes, and range from 11 to 110  $^{\circ}\text{C/Ma}$  (circles in Fig. 3b). Pyroxene and hornblende may yield high cooling rates due to the loss of rim material during separation (see above). The equilibrium fraction-

ation factor for biotite is not well known, so that the biotite intersection is not very well constrained. It was noted that much of the magnetite would occur as inclusions in the pyroxene. If the pyroxene acted to isolate the included magnetite from other minerals, exchange would not occur during cooling. Figure 3b shows this effect. The open star at 10  $^{\circ}\text{C/Ma}$  shows what the  $\delta^{18}\text{O}$  value of the magnetite would be in that case. It is possible that "armouring" of some of the magnetite would result in a mixture of magnetites whose average value would fall between the star and the model line.

The garnet indicates that the cooling rate has been approximately 0.1  $^{\circ}\text{C/Ma}$ . Most probably small magnetite intergrowths in the garnet are the reason of this result. Given the geochronological data for these rocks, another possibility would be that garnet was formed during a post intrusive heating at approximately 1810 Ma. The  $T_c$  for the garnet of this size, when cooled at 0.1  $^{\circ}\text{C/Ma}$ , is 690  $^{\circ}\text{C}$ . The garnet could have formed at a temperature somewhat below that value, 1810 Ma ago, being in equilibrium with the whole rock. This would imply that the 1810 Ma heating has attained garnet grade temperatures resetting the 1850 Ma K-Ar

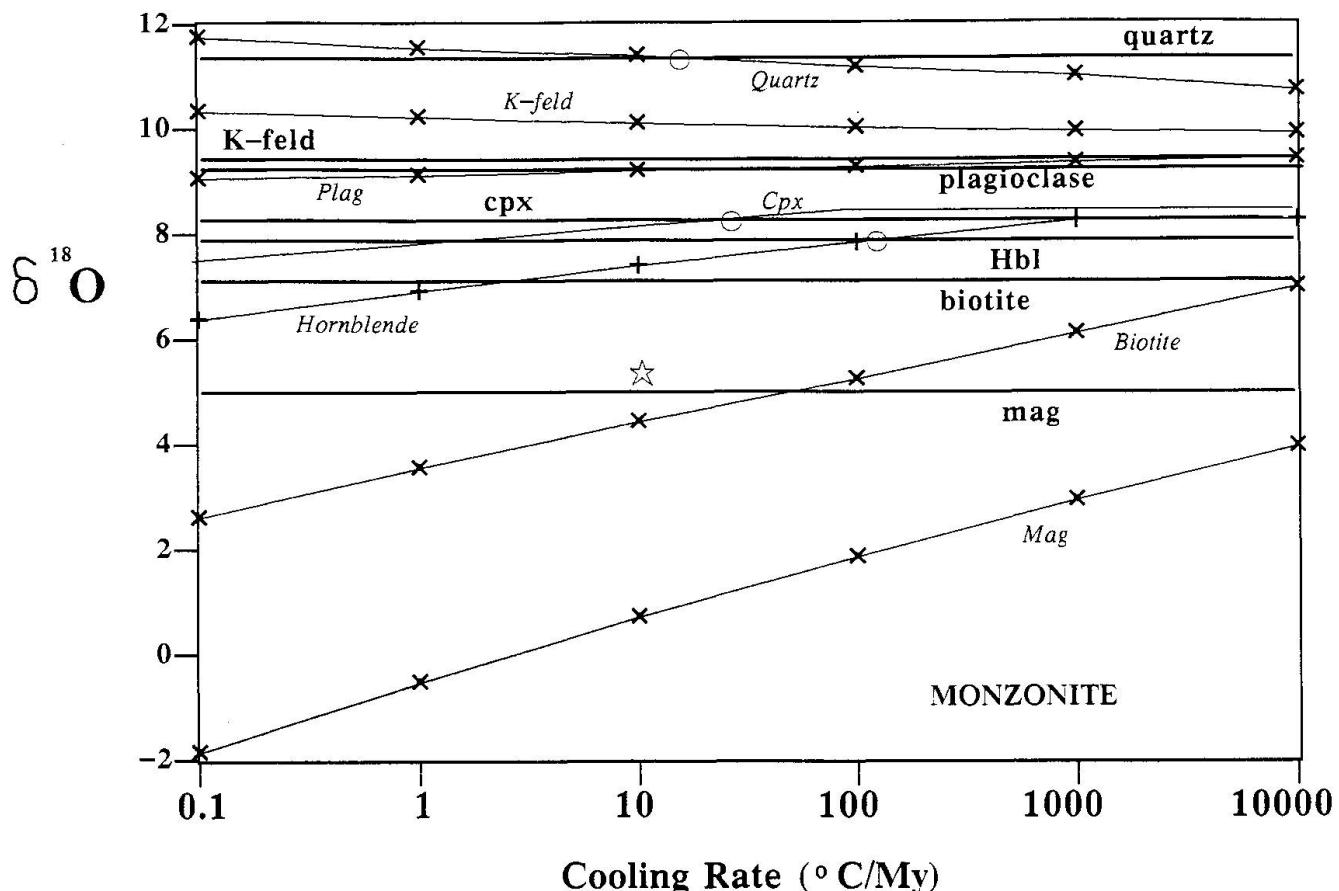


Fig. 3b Graph of the cooling rate calculations for the monzonite sample giving the measured (bold lines) and the calculated (thin lines)  $\delta^{18}\text{O}$  values and the corresponding cooling rates (open circles). The open star corresponds to the value calculated for the magnetite "armoured" by the pyroxene.

hornblende age (HÖLTTÄ et al., in prep.) and possibly the U-Pb monazite age (SALLI, 1983) which is not the case.

## 5. Discussion

The Vaaraslahti mangerite intruded and contact-metamorphically overprinted its host-rock 1884 Ma ago (SALLI, 1983). A rather moderate cooling rate is indicated by the 1874 Ma (SALLI, 1983) monazite age. Assuming a closure temperature of approximately 650–700 °C for the monazite (U-Pb) and an intrusion temperature of  $900 \pm 100$  °C for the mangerite a cooling rate of  $25 \pm 15$  °C/Ma would result for the first 10 Ma. Assuming a constant cooling rate of 25 °C/Ma the rock would have subsequently cooled to 300 °C at 1850 Ma. K-Ar biotite ages of 1770–1790 Ma for the granite and its host-rock contradict this calculation. The complex must have seen either a postmagmatic reheating in the time interval between 1870 and about 1790 Ma or a reduction of the mean cooling rate to only 3.5 °C/Ma (900–300 °C), e.g. a decrease of the cooling rate with time.

The Rb-Sr isochron data refine this interpretation. The mineral system reequilibrated at approximately 1810 Ma ago, at least with respect to the feldspars. This suggests that the rock was either maintained at a relatively high temperature for a long time, or a second heating occurred at approximately 1810 Ma. This date can also be related to the 1800–1820 Ma amphibolite facies metamorphism and granite intrusion reported for southeastern Finland (KORSMAN et al., 1984; VAASJOKI and SAKKO, 1988).

As seen in the oxygen data, there is no evidence that the resetting of the strontium system involved meteoric water. Any fluid needed for metamorphic reactions or strontium reequilibration has come from the mangerite itself, or a similar  $\delta^{18}\text{O}$  source. The biotite-producing reactions might, therefore, be part of the strontium re-equilibration, the Rb-Sr mineral isochron would define a minimum for their age. Return now to the monzonite oxygen data to examine what effect a post intrusive heating would have on those isotopic compositions. It is likely that the pyroxene and its included magnetite would have remained closed systems and unchanged. Hornblende and quartz might have exchanged oxy-

gen isotopes to some degree while the other minerals would have exchanged oxygen isotopes. Consequently, the basis for assuming a cooling rate of about 50 °C/Ma is the pyroxen, the quartz and possibly the hornblende. The number of useful minerals is, therefore, too small to infer a cooling rate with any precision. It is possible that the rate was 10 to 50 °C/Ma, but this is a tenuous conclusion. It is consistent with the other data, however.

The Rb–Sr and K–Ar biotite ages differ by 30 Ma. This difference may be due to low temperature diffusional strontium exchange, where the closure temperature for the strontium volume diffusion would be somewhat lower than the blocking temperature of 300 °C used for the K–Ar system in the biotite. This result would support the theory of a continuously decreasing cooling rate from about 50 to around 0.5–1 °C/Ma between 1880 and 1750 Ma. The cessation of the last strontium equilibration between the feldspars at 1810 Ma could be attributed to a temperature of about 500–550 °C for the slow cooling rate. Based on hornblende and biotite K–Ar blocking temperatures and their implied cooling path, a temperature of about 400 °C could be interpolated for the reequilibration of strontium between the feldspars. The discrepancy between the interpolated and calculated cooling temperatures may be attributed to the reheating of the system at 1810 Ma to temperatures exceeding the feldspar closure, but then the K–Ar hornblende age may be explained by an incomplete reset, e.g. excess argon in the hornblende lattice.

## 6. Conclusions

- Mineral and whole-rock oxygen analyses reveal "normal" plutonic values.
- The influence of meteoric water to the cooling system can be excluded.
- Post intrusive reactions (hornblende to biotite, myrmecitisation of feldspars) can be referred to a fluid being restricted to the intrusion or having similar  $\delta^{18}\text{O}$  characteristics.
- Pyroxene, hornblende and quartz oxygen data indicate a cooling rate on the order of 30 °C/Ma, with an uncertainty of a factor of 3.
- Rb–Sr feldspar isochron ages postdate the intrusion and can be correlated to metamorphic and plutonic events dated in south-eastern Finland.
- The Rb–Sr age of the biotite is somewhat lower than the corresponding K–Ar age.

The Vaaraslahti intrusive may have cooled at a rate of 10 to 50 °C/Ma at high temperatures, e.g. during about the first 10 Ma. Secondary reactions of pyroxene and hornblende forming biotite at their margins may be attributed to low temperature

reequilibration of the system or a post intrusive thermal event. Feldspar and biotite Rb–Sr ages imply a decreasing cooling rate to about 1 °C/Ma at low temperatures as calculated from the K–Ar results (HAUDENSCHILD, 1988). Strontium diffusion data suggests a strontium closure temperature of 500–550 °C for the feldspars, and the strontium exchange between biotite and other phases (apatite?) to cease at a temperature somewhat below the 300 °C blocking temperature of the K–Ar system.

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