Stellerite and Sr-containing stilbite in granitic rocks from the Siljan Ring structure, central Sweden

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Morad, S., Filippidis, A., AlDahan, A.A., Collini, B. and Ounchanum, P. 1989 08 31: Stellerite and Sr-containing stilbite in granitic rocks from the Siljan Ring structure, central Sweden. *Bulletin of the Geological Institutions of the University of Uppsala*, N.S. Vol. 12, pp. 143–149. Uppsala. ISSN 0302-2749.

Stellerite (a = 13.632 Å, b = 18.162 A, c = 17.872 Å, V = 4425 $Å^3$, ß = 90°, $Na_{0.20}Ca_{3.70}$-$Al_{7.88}Si_{28.09}O_{72} \cdot 30.9H_20$) and Sr-containing stilbite (a = 13.644 Å, b = 18.176 Å, c = 11.246 Å, V = 2206 $Å^3$, ß = 127⁰73', $Na_{0.56}K_{0.13}Ca_{2.48}Mg_{1.13}Sr_{0.31}Al_{9.02}Si_{27.03}O_{72} \cdot 33.5H_2O$) occur in granites of the Siljan Ring structure, central Sweden. This structure was caused by a meteorite impact in Late Devonian (368 Ma). The zeolites fill fractures and amygdules and replace mainly plagioclase. They are due to hydrothermal solutions (70–100°C) related to meteoric waters that entered the granite along fractures caused by the old tectonism and the meteorite impact.

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Introduction

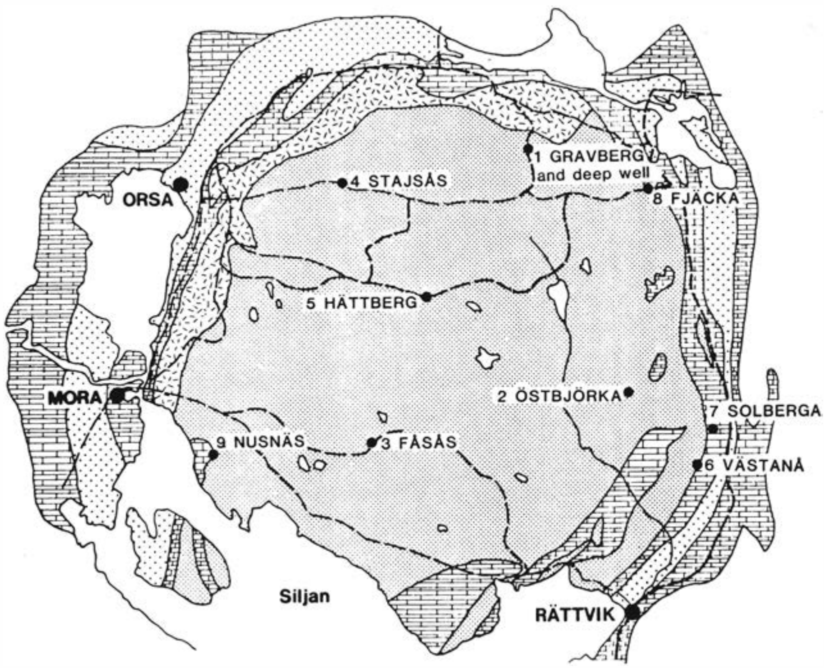
The occurrence of stilbite and stellerite was reported mainly from volcanic rocks and volcanogenic sediments (e.g., Coombs et al. 1959, Hay 1966, Seki et al. 1969, Galli & Passaglia 1973, Akizuki & Konno 1985, Keith & Staples 1985). These minerals as well as other zeolites are important indicators of T–P conditions and thus very useful for the evaluation of parageneses and crystallization chronology in rocks. This study mainly aims at describing the chemistry, texture and paragenesis of stilbite and stellerite in relation to other minerals in granitic rocks of the Siljan Ring structure, central Sweden (Fig. 1). This structure is a remnant of a meteorite-impact crater (e.g., Svensson 1973, Grieve 1988). Postorogenic (1.65–1.75 Ga) Dala granites occupy the central (c. 32 km in diameter) part of the ring structure. Zeolite-containing core samples of Dala granites were collected from shallow (≤600 m deep) boreholes and some samples from cores and cuttings from the deep well at Gravberg (Fig. 1). The zeolites described in this paper were sampled from borehole no. 4 at a depth of 401.08–401.15 m.

Polished thin sections were prepared for petrographic examination and microprobe analyses (after coating with a thin layer of carbon). The microprobe used was a ARL-EMX instrument which employs the ZAF-4 correction program. Small sample chips (~15 mm in size) were coated with a thin layer of gold and examined by a JEOL JSM840 scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyser (EDS) and a backscatter electron mode (BSE). The BSE examination was performed on the carbon-coated thin sections. Vein-filling zeolitic material was hand-picked, powdered and examined by a Phillips X-ray diffractometer using Ni-filtered CuK_α radiation. The unit-cell parameters were calculated using a computer program (N.O. Ersson, Department of Inorganic Chemistry, Uppsala University; unpublished).

Brief microscopic description of the rocks

The granites of the Siljan area are generally medium to coarse grained, partly porphyritic and reddish to greyish red. They vary from two-feldspar granite over adamellite to granodiorite in composition (cf. Hughes 1982).

Hydrothermal alterations of the rocks investigated are either replacement of primary minerals or fillings of fractures. The most common replacement features are albitisation of primary K-feldspar and



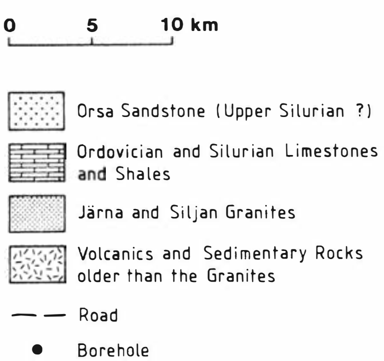


Fig. 1. Bedrock map of the central part of the Siljan Ring structure (simplified after Hjelmqvist 1966), showing location of the boreholes.

plagioclase, sericitisation of mainly plagioclase, chloritisation of biotite and hornblende and hematitisation of Fe-Ti oxides. In most such alternations, fine crystals ($\leq$20 μm) of quartz, titanite, hematite, rutile and epidote occur. At depths less than 1000 m, smectite and calcite occur within the altered feldspars. Pumpellyite and prehnite are observed in altered biotite and chlorite at depths greater than 3500 m (AlDahan 1988).

The most common fracture-filling minerals are quartz, epidote, chlorite, calcite and leucoxene (fine TiO_2 crystals). At depths less than 1000 m, stilbite and stellerite together with chlorite, smectite and calcite are found in some fractures. More details of the general alterations in the rocks investigated are given in AlDahan (1988).

Mode of zeolite occurrence

Stilbite and stellerite in the granitic rocks investigated occur predominantly as fractures and, less commonly, as amygdule fillings (Fig. 2). These zeolites appear as euhedral crystals (~30−120 μm across) usually intimately intergrown with each other (Figs. 2B and 2C); small amounts of hematite are commonly admixed (Fig. 2C). In some cases, the fracture wall is aligned by calcite, chlorite and/or smectite whereas the zeolites occupy the central part of the fracture.

Stilbite and stellerite are also found as minor replacements in altered feldspars in the host granite. Replacement of feldspars by the zeolites could sometimes be random and the contact between the

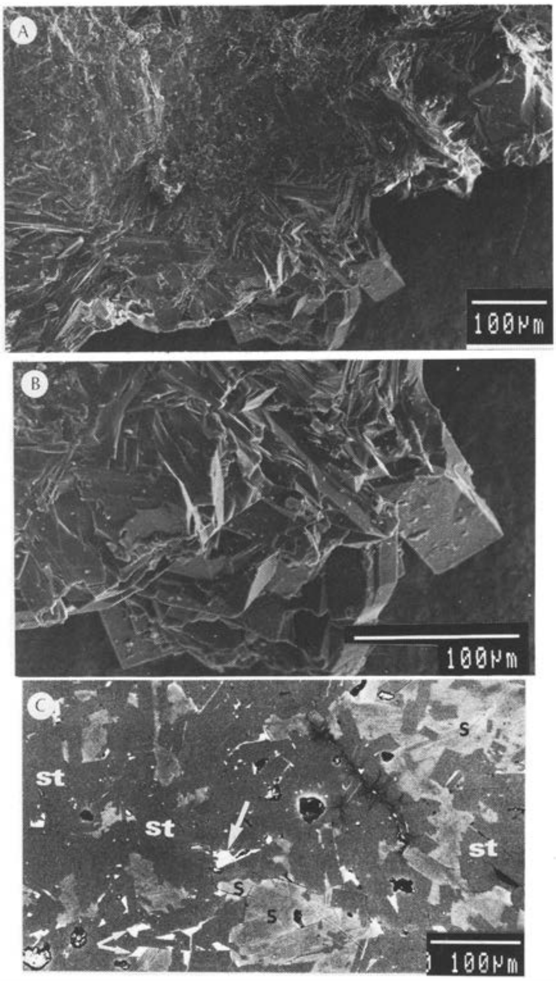


Fig. 2. A – SEM micrograph of fracture-filling zeolites.
B – A higher magnification of part of Figure 2A.
C – BSE image showing the intergrowth of stilbite (s) and stellerite (st); arrows show hematite.

zeolites and replaced feldspar is obscured (on the scale of the SEM; Fig. 3A) or sharp (Fig. 3B). In a few cases, the replacive zeolites display a somewhat locally preferred two-directional orientation in partly altered feldspars. The zeolites were also observed in a few biotite grains which are severely altered into chlorite and/or smectite.

Chemistry and X-ray diffraction data of stellerite and stilbite

The microprobe analyses of stellerite and stilbite are presented in Table 1. These analyses are for frac-

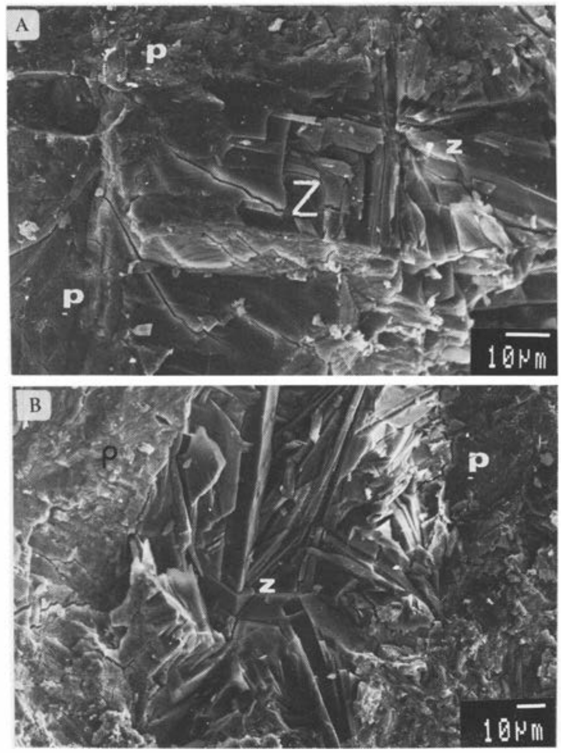


Fig. 3. A – Zeolite (z) replacing plagioclase (p). Note the obscured boundary between the two minerals.
B – Zeolite (z) filling voids in an altered plagioclase (p).

ture-filling varieties, because the commonly fine crystalline nature of stellerite and stilbite replacing feldspars and biotite hindered an accurate microprobe analysis.

Stellerite compared to stilbite shows higher amounts of SiO_2 and CaO but lower Al_2O_3, MgO, SrO, Na_2O and K_2O contents. SrO contents (average 1.1 wt.%) found in the stilbite, are higher than those of stilbites reported in the literature (Filippidis et al. 1988).

The chemical parameter $R = Si/(Si+Ti+Al+Fe^{3+})$ which represents the percentage of the tetrahedra occupied by Si is, on average, 0.780 (0.776–0.784) for stellerite and 0.748 (0.747–0.749) for stilbite. Based on the R-values, the stellerite investigated is classified as "acid zeolite" ($R>0.75$) while the Sr-containing stilbite is classified as "intermediate zeolite" ($0.625<R<0.75$) after Gottardi (1978).

Based on the cation proportions of 72 oxygen atoms, the formula for stellerite is $Na_{0.20}Ca_{3.70}Al_{7.88}Si_{28.09}O_{72} \cdot 30.9H_2O$ and for stilbite $Na_{0.56}K_{0.13}Ca_{2.48}Mg_{1.13}Sr_{0.31}Al_{9.02}Si_{27.03}O_{72} \cdot 33.5H_2O$. Variations in the Mg–Ca–(Na+K) contents of stil-

Table 1. Microprobe analyses of stellerite (1–3) and stilbite (4 and 5).

Analysis No.	1	2	3	4	5	Average stellerite	Average stilbite
SiO_2 wt.%	59.09	59.57	57.73	55.20	55.24	58.80	55.22
TiO_2	0.04	0.00	0.00	0.00	0.06	0.01	0.03
Al_2O_3	14.39	13.78	13.82	15.72	15.56	14.00	15.64
Fe_2O_3[1]	0.04	0.23	0.05	0.17	0.11	0.11	0.14
MnO	0.10	0.17	0.00	0.00	0.02	0.09	0.01
MgO	0.21	0.07	0.00	1.43	1.66	0.09	1.55
CaO	7.38	7.16	7.12	4.79	4.65	7.22	4.72
SrO	0.00	0.06	0.00	1.08	1.10	0.02	1.09
BaO	0.00	0.00	0.19	0.25	0.29	0.06	0.27
Na_2O	0.45	0.09	0.09	0.56	0.62	0.21	0.59
K_2O	0.00	0.09	0.00	0.20	0.22	0.03	0.21
H_2O*	18.30	18.78	21.00	20.60	20.47	19.36	20.53
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Si	27.904	28.243	28.135	27.029	27.025	28.094	27.026
Ti	0.014	–	–	–	0.022	0.004	0.011
Al	8.009	7.700	7.938	9.072	8.972	7.884	9.021
Fe^{3+}	0.014	0.082	0.018	0.063	0.040	0.040	0.052
Mn	0.040	0.068	–	–	0.008	0.036	0.004
Mg	0.148	0.049	–	1.044	1.210	0.064	1.131
Ca	3.734	3.637	3.718	2.513	2.437	3.696	2.475
Sr	–	0.016	–	0.307	0.312	0.006	0.309
Ba	–	–	0.036	0.048	0.056	0.011	0.052
Na	0.412	0.083	0.085	0.532	0.588	0.195	0.560
K	–	0.054	–	0.125	0.137	0.018	0.131
H_2O	28.823	26.697	34.133	33.642	33.401	30.851	33.512
Z	35.941	36.025	36.091	36.164	36.059	36.022	36.110
X	4.334	3.907	3.839	4.569	4.748	4.026	4.662
D	3.922	3.770	3.754	3.912	4.023	3.813	3.971
M	0.412	0.137	0.085	0.657	0.725	0.213	0.691
R	0.776	0.784	0.780	0.747	0.749	0.780	0.748

[1] Fe_2O_3 = total iron
* Estimated by difference
Z = Si+Ti+Al+Fe^{3+}, X = Mn+Mg+Ca+Sr+Ba+Na+K, D = Mn+Mg+Ca+Sr+Ba, M = Na+K,
R = Si/(Si+Ti+Al+Fe^{3+})

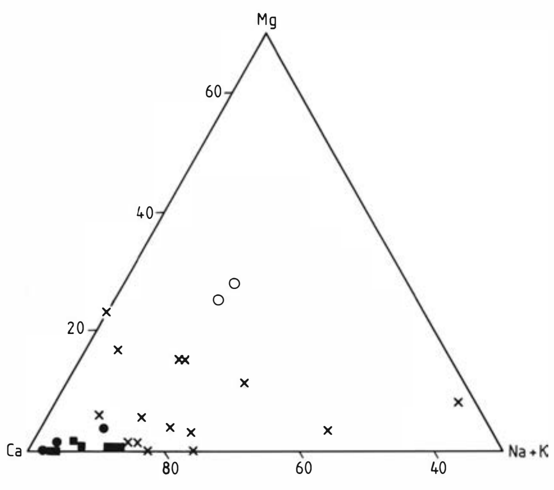


Fig. 4. A triangular Mg–Ca–Na+K plot of the stilbites (o) and stellerites (•) studied.
■ = Stellerites from Galli & Passaglia (1973), Filizova et al. (1975), Alberti et al. (1978), Passaglia et al. (1978).
x = Stilbites from Heflik (1964), Aumento (1966), Galli & Gottardi (1966), Harada & Tomita (1967), Wise (1969), Abbona & Franchini (1970), Simonot-Grange et al. (1970) Slaughter (1970), Liou (1971), Filizova et al. (1975), Zabinski (1975), Filippidis et al. (1988).

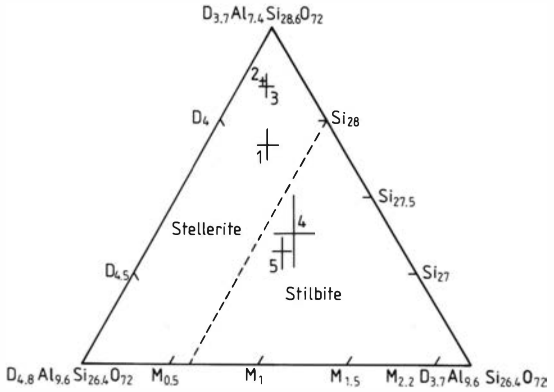


Fig. 5. The triangular mole plot $D_{3.7}Al_{7.4}Si_{28.6}O_{72}$ – $D_{4.8}Al_{9.6}Si_{26.4}O_{72}$ – $M_{2.2}D_{3.7}Al_{9.6}Si_{26.4}O_{72}$ (after Passaglia et al. 1978). The dashed line separates the fields of stellerite and stilbite. 1, 2 and 3 = stellerite; 4 and 5 = stilbite of Table 1. M = Na+K; D = Mn+Mg+Ca+Sr+Ba.

bite and stellerite are shown in Figure 4. Variations in the D (divalent cations) –M(monovalent cations)–Si content of the investigated zeolites are shown in Figure 5, using the triangular mole plot $D_{3.7}Al_{7.4}$-$Si_{28.6}O_{72}$–$D_{4.8}Al_{9.6}Si_{26.4}O_{72}$–$M_{2.2}D_{3.7}Al_{9.6}$–$Si_{26.4}$-$O_{72}$ of Passaglia et al. (1978).

The unit-cell parameters of stellerite and Sr-containing stilbite studied are listed in Tables 2 and 3, together with some data from the literature. No significant variations are observed for the cell-parameter values with respect to those reported by the other authors. The cell parameters of stellerites and stilbites have been correlated with the following chemical variables: Z = Si+Ti+Al+Fe^{3+}, X = Mn+Mg+Ca+Sr+Ba+Na+K, D = Mn+Mg+Ca+Sr+Ba (divalent cations), M = Na+K (monovalent cations), Z/X, M/X, Na and K. For stellerite the correlations of the cell parameters with these chemical variables show broad scattering. For stilbite, the correlations of the cell parameters b, V and ß with chemical composition show broad scattering, whereas the parameters a and c are positively correlated with X, M, M/X and negatively with Z/X. These correlations show that the divalent cations do not affect the parameters a, b, c, V and ß. The same results for stilbite correlations are presented by Filippidis et al. (1988) and were used for the present stilbite correlations, except those of Sr-containing stilbite.

Discussion

Experimental studies of Liou (1971) and Juan & Lo (1973) suggest that stilbite crystallizes at temperatures lower than 180°C. Harada & Tomita (1967) re-

Table 2. Cell parameters of stellerite (orthorhombic).

a (Å)	b (Å)	c (Å)	V(Å^3)	ß^o	Reference
13.599	18.222	17.863	4426	–	Galli & Passaglia (1973)
13.605	18.196	17.842	4417	90	Alberti et al. (1978)
13.599	18.224	17.863	4427	90	Passaglia et al (1978)
13.589	18.228	17.841	4419	90	-"-
13.591	18.221	17.840	4418	90	"-"
13.600	18.199	17.838	4415	90	-"-
13.595	18.244	17.843	4426	90	-"-
13.632	18.162	17.872	4425	90	This study

Table 3. Cell parameters of stilbite (monoclinic).

a (Å)	b (Å)	c (Å)	V(Å^3)	ß^o	Reference
13.681	18.182	11.300	2159.5	129.8	Aumento (1966)
13.64	18.24	11.27	2209.5	128	Galli & Gottardi (1966)
13.595	18.306	11.238	2223.9	127.33	Wise (1969)
13.62	18.16	11.25	2206.2	127.35	Abbona & Franchini (1970)
13.64	18.24	11.27	2209.5	128	Simonot-Grange et al. (1970)
13.69	18.25	11.31	2220.6	128.2	Slaughter (1970)
13.58	18.31	11.25	2183.1	128.7	Liou (1971)
13.607	18.259	11.286	2210.7	127.96	Filippidis et al. (1988)
13.601	18.252	11.282	2208.8	127.94	-"-
13.644	18.176	11.246	2206	127.73	This study

ported that above 200°C and water pressures >40 atm stilbite produces wairakaite. The relatively low Na and K contents of the investigated zeolites as well as their association with smectite suggest a maximum temperature of <100°C (Velde 1985). Fluid-inclusion data on quartz from the present mineral paragenesis, indicate a minimum trapping temperature of ~130°C and a minimum homogeneization temperature of ~100°C (Komor et al. 1988). Stable isotopic data ($\delta^{18}O$ and $\delta^{13}C$) on fracture-filling calcite from the present mineral paragenesis indicate a formation temperature as low as 70°C (Valley et al. 1988). Stilbite formed at a temperature of about 70°C in hot springs was reported by Coombs et al. (1959)

Microscopic observations indicate that stilbite usually occurs as relicts within the stellerite (Fig. 2C). In other words, stilbite crystallized first and was then replaced by stellerite due to changes in pore-solution chemistry (increase in activity of Ca^{2+} and decrease in activities of Na^+, K^+, Sr^{2+} and Mg^{2+}) and perhaps temperature. This replacement is aided by crystal-structural similarities between these two zeolites (cf. Harada & Tomita 1967, Alberti et al. 1978). The presence of hematite with these zeolites (Fig. 2C) indicates that their genesis is related to oxygenated solutions and thus supports the hypothesis of formation by fluids related to meteoric waters (cf. AlDahan 1988).

The replacement of plagioclase (average composition from six microprobe analyses) by stilbite and stellerite can be tentatively expressed as follows:

(1) $$8.35\,\underbrace{(Na_{0.91}K_{0.01}Ca_{0.05}Mg_{0.01}Sr_{0.02})\,Al_{1.08}Si_{2.91}O_8}_{\text{plagioclase}} + 27.78H_2O + 2.06Ca^{2+} + 0.05K^+ + 2.73H_4SiO_4 + 0.14Sr^{2+} + 1.05Mg^{2+} + 0.52H^+ = \text{stilbite} + 7.04Na^+$$

and

(2) $$7.30\text{plagioclase} + 7.10H_2O + 3.34Ca^{2+} + 6.85H_4SiO_4 + 0.20H^+ = \text{stellerite} + 6.44Na^{2+}\ 0.07\,K^+ + 0.07Mg^{2+} + 0.15Sr^{2+}.$$

The Na^+ released through the above reactions might have been used in the albitisation of K-feldspar, a process that is very common in Siljan Ring granites (AlDahan 1988).

Besides the replacement by zeolites, the plagioclase is also replaced by sericite. This replacement phenomenon occurs in most of the granites in the Siljan Ring structure and is believed to predate the formation of zeolites (AlDahan 1988). Replacement of plagioclase by smectite, on the other hand, has taken place more or less simultaneously with replacement by zeolite. The alternation of biotite into sericite, green-coloured chlorite or both is apparently simultaneous with the formation of zeolites. This reaction is most common at shallow depths, whereas chloritisation of biotite increases with depth. Mg and Si ions liberated from the above alteration could have been used in the replacement of plagioclase by zeolites.

The occurrence of highly hydrous zeolites at relatively shallow depths in the granites studied, suggests formation through alteration of granitic rocks by hydrothermal fluids of low temperature (70–100°) related to meteoric waters (cf. AlDahan 1988, Valley et al. 1988). These were introduced partly as a result of fracturing by the meteorite impact.

Acknowledgements. – Thanks are due to Prof. G. Christofidis for critical comments on the manuscript. O. Wallner took great care in making the thin sections.

Finally, we thank Mr. Tord Lindbo, project leader of the Deep Gas Project of the Swedish State Power Board and Managing Director of DDP AB, for putting the material at our disposal.

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Printed by Ekenäs Tryckeri Ab, Ekenäs, Finland August 31th, 1989