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Preliminary Palaeozoic Sm-Nd ages of fluorite-calcite-galena veins in the southeastern part of the Fennoscandian Shield

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

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1 Introduction

Fluorite-calcite-galena-bearing veins are common in the margins of the Fennoscandian Shield, particularly along the Caledonian front and in the Baltic Sea region. In a previous SKB report /Alm and Sundblad 2002/, the geological characteristics of fluorite-calcite-galena-bearing veins in the Baltic Sea region were presented together with the results of fluid inclusion and lead isotope work. The main conclusions were that these veins represent a regionally important mineralized system, which was formed during the Phanerozoic from low-temperature (60–190°C) hydrothermal fluids, and that a number of components, e.g. Ca, F, and Pb, were derived from the Precambrian crystalline basement.

Even if a Phanerozoic timing could be deduced for the fluorite-calcite-galena system, adequate interpretations in a geodynamic perspective will be limited until better time constraints for the hydrothermal event are established. An effort to date these veins by applying the Sm-Nd isotope technique to fluorite was therefore initiated during 2003. Although the Sm-Nd isotope method is well established for rocks and silicate minerals, no documented efforts to apply this technique on Fennoscandian fluorites are known to us. Thus, the present study has a pioneer character and the activities during 2003 can be considered both as a method development and a result-oriented investigation.

2 Geological background

Veins containing fluorite, calcite and galena are identified at a number of sites in Sweden, Norway, Finland and northwestern Russia (Figure 2-1). These mineralizations occur as mm-thin, or occasionally cm-dm-wide, fracture infillings in vertical to subvertical structures in Precambrian crystalline rocks of any age and composition all over the Fennoscandian Shield. The veins are typically located close to overlying platform cover of Late Precambrian or Cambrian sedimentary rocks. The veins are therefore mainly located along the margins of the shield (e.g. along the Caledonian Front, in southeastern Sweden, in the Åland region and along the Gulf of Finland) but a few occurrences are spatially related to inliers of Cambro-Silurian sediments under the Bothnian Sea and the Gulf of Bothnia. Geological and textural relations between the fluorite-calcite-galena veins and Cambrian sandstone dykes indicate that the vein-forming processes must post-date the Early Cambrian. The close relation to the base of the Palaeozoic cover sequence also indicates that the veins formed immediately under the subcambrian peneplane. The absence of associated magmatic rocks indicates that the veins were formed by geological processes that were independent of magmatic activity. This fluorite-calcite-galena association thus represents a distinct mineralization type, which should not be confused with e.g. the fluorite-calcitegalena veins associated with the Permian Oslo Palaeorift and coeval dolerites in Skåne. Fluid inclusion data on fluorite veins in the Baltic Sea region /Alm and Sundblad 2002/ indicate deposition from high-saline (15–26 eq wt % CaCl₂-NaCl) fluids at temperatures of 60–190°C, which are significantly lower than for the magmatogenic hydrothermal veins in the Permian Oslo Palaeorift.

The fluorite-calcite-galena veins show variable compositions, both with respect to mineral parageneses and lead isotopic compositions. Some are dominated by fluorite, others by calcite and yet others (more seldom) by galena, but all three of these minerals are commonly identified in various proportions at each locality. The lead isotopic composition is radiogenic ($^{206}Pb/^{204}Pb$ ratios > 17.0), in most cases with negative model ages, which is typical for Phanerozoic derivation of lead from Precambrian crustal sources. The variations in ²⁰⁶Pb/²⁰⁴Pb ratios reflect specific geochemical signatures with respect to U, Th and Pb in the source rocks. The least radiogenic compositions (²⁰⁶Pb/²⁰⁴Pb ratios from 17.0 to 18.6) are related to U- and Th-depleted sources in highly metamorphosed Archaean and Early Proterozoic gneisses, whereas other veins, hosted by various Proterozoic rocks, have ²⁰⁶Pb/²⁰⁴Pb ratios ranging from 19 to 35. The highest ²⁰⁶Pb/²⁰⁴Pb ratios are recorded for the Tindered veins, which are hosted by rocks with high U contents and high U/Pb ratios /Alm and Sundblad 2002/. The lead isotopic composition thus supports a Phanerozoic age of the veins but is also an indication of a local source for the lead (i.e. host rock appears to be source rock). Such a link between host rock geochemistry and vein character is also documented for fluorine; abundant fluorite is only found in veins hosted by rocks with an elevated fluorine content, allowing for fluorite to be part of the magmatic paragenesis.

Based on the textural and geological relations between fluorite veins and Cambrian sandstone dykes as well as the lead isotopic systematics, the timing of the mineralizing event has thus been constrained to the Phanerozoic. Several speculations on a more specific timing of the vein formation include Cambrian /Sundblad and Alm 2000/, Caledonian (Silurian/Devonian; /Johansson 1983/) and Permian ages, but these are all based on weak arguments and thus very uncertain. The timing of the mineralizing event is therefore still the weakest point when trying to establish a coherent genetic model for this mineralization type and associated fracture systems. To create more realistic geological models for the vein emplacement, a much better control of the timing for the hydrothermal activity is necessary.



Figure 2-1. Geology of the Fennoscandian Shield with location of the investigated areas $(G = G\"{o}temar, T = Tindered, L = Lovisa)$ together with other relevant fluorite-calcite-galena mineralizations.

3 Background to the Sm-Nd isotope method for dating fluorite

Fluorite may carry ppm levels of Sm and Nd (replacing Ca in the fluorite lattice), and more or less successful efforts to determine the age of fluorite by the Sm-Nd isochron method are reported for Phanerozoic mineralizations /Galindo et al. 1994, Chesley et al. 1991, 1994, Menuge et al. 1997/. The procedure is to analyze the isotopic composition of Sm and Nd in some 3–6 fluorite samples within a mineralized system, so that the ¹⁴³Nd/¹⁴⁴Nd ratio of each sample can be plotted vs the ¹⁴⁷Sm/¹⁴⁴Nd ratio in a standard Sm-Nd isochron diagram. An important prerequisite is that all samples have the same initial ¹⁴³Nd/¹⁴⁴Nd ratio in order to allow for a meaningful age calculation.

4 Present investigation

In the present investigation, fluorite veins were selected in three geological settings in the Baltic Sea region; 1) Götemar, in a 1,452 Ma granite in southeastern Sweden, 2) Tindered, in 1,859 Ma granitic gneisses along the northeastern margin of the Transscandinavian Igneous Belt (TIB) complex in southeastern Sweden and 3) Lovisa, in the c 1,640 Ma Wiborg batholith in southeastern Finland; the various rocks are described below. All three mineralized systems have most probably formed semicontemporaneously as a result of large-scale Phanerozoic processes. All veins have been studied with regard to petrology, structures and fluid inclusion systematics, which indicate mineral deposition along vertical fractures at moderate depths. The lead isotopic composition of associated galena suggests that the elements in the vein minerals were derived from the host rock granites. Since the geochemical signature of each host rock is distinct, and previous studies of the sources to the vein material have demonstrated large variations with respect to their host rock, variations in the Sm and Nd contents in the fluorite are also expected at respective site. Hence, three parallel isochrons were anticipated as a result of the present investigation.

1) Götemar

The anorogenic Götemar granite has a diameter of five km and is located 30 km northeast of Oskarshamn (Figures 2-1, 4-1 and 4-2). This pluton is dominated by a coarse, evengrained granite with a SiO₂ content exceeding 70 wt %, a total alkali-oxide content of 8.8 wt % and about 0.5% F, and fluorite as well as F-rich biotite is documented /Kresten and Chyssler 1976, Alm and Sundblad 2002/. Subhorizontal fluorite- and topaz-bearing pegmatites, dominated by quartz, K-feldspar and phlogopitic mica, are locally found within and outside the pluton /Kresten and Chyssler 1976/. Several age determinations employing different minerals and different methods have been carried out on the Götemar pluton /Åberg et al. 1984, Smellie and Stuckless 1985, Åberg 1988/ but the best age estimate is 1,452 +11/-9 Ma, obtained by /Åhäll 2001/. Mm-dm-wide vertical Cambrian sandstone dykes are abundant in the eastern part of the pluton, particularly in the Kråkemåla 2 quarry, and fluorite veins are observed in many of the quarries in the Götemar granite, including Askaremåla, Kråkemåla 1–2, Bussvik and Götebo. Fluorite veins are also found in the older TIB rocks immediately outside the Götemar pluton. /Alm and Sundblad 2002/ considered the fluorite vein mineralizations to be caused by Phanerozoic redistribution of elements from the Götemar pluton. /Kresten and Chyssler 1976/ paid particular attention to the fact that the dykes with Cambrian sandstone only were found east of the fault seen in Figure 4-2, and concluded a post-Cambrian age for this structure. The fault is of more than local importance, because it continues for at least 20 km towards the north /Kresten and Chyssler 1976, Lundegårdh et al. 1985/.



Figure 4-1. Geology of the northern part of Kalmar county with location of Götemar and Tindered, together with other relevant fluorite-calcite-galena mineralizations.



Figure 4-2. Geology of the Götemar area /Kresten and Chyssler 1976/ with location of investigated samples.

2) Tindered

The Tindered granite is an informal name for a characteristic rock unit occurring along the border between the TIB and the metamorphosed Svecofennian complex, some 30 km north-west of Västervik (Figures 2-1 and 4-1). This in part strongly deformed granite was marked as "Older granite" and "Older granite and granodiorite, porphyritic" by /Lundegårdh et al. 1985/ on the 1:250,000 map sheet of the region. Recent work on this unit has shown that it has an age of 1,859 Ma (H Wikman, SGU Lund, pers comm 2004) and that two main rock units can be distinguished: "biotite granite" and "porphyritic granite" /Alm and Sundblad 2002/. Both units are metaluminous, differentiated granites according to their geochemical signatures. The fluorine content ranges from 0.22 to 0.25% in the biotite granite and is slightly lower (c 0.18%) in the porphyritic granite. Fluorite has been documented in both granite varieties /Alm and Sundblad 2002/. The fluorite veins at Tindered are abundant in the exposures along the main road (Figure 4-3) and one vein is associated with Cambrian sandstone dykes.



Figure 4-3. Geology of the Tindered area /Alm and Sundblad 2002/ with location of investigated samples.

3) Lovisa

The Wiborg batholith is located in southeastern Finland and in adjoining areas in Russia (Figure 2-1). It is the largest of the Fennoscandian rapakivi plutons and was emplaced from 1,650 Ma to 1,625 Ma /Vaasjoki et al. 1991/. The pluton consists of several rock types, including wiborgite (with spectacular mantled feldspars), pyterlite, coarse- and even-grained rapakivi as well as porphyry aplite. The chemical character of the rocks in the Wiborg batholith is typical for A-type granites and the contents of fluorine is often so high that fluorite has formed in the magmatic rock in addition to F-rich biotite /Alm and Sundblad 2002/. Vertical fracture infillings with fluorite have been observed at two localities east of Lovisa (Figure 4-4): 1) Metsola, on the main road between Lovisa and Kotka, some 8-10 km east of Lovisa and 2) Hästholmsvägen, some 3 km southeast of Lovisa, on the road connecting Lovisa with the nuclear power plant at Hästholmen. These fluorite veins are located on the map sheets 3023 Kotka and 3021 Porvoo but were not recognized when /Laitala 1964/ and /Simonen and Laitala 1970/ published their respective bed rock map. The Metsola fluorites are located in a narrow lens of pyterlite, only few hundred metres from surrounding varieties of wiborgite and some 1-2 km east of an even-grained rapakivi variety. The Hästholmsvägen fluorites are located on the border between a wiborgite and a porphyry aplite.



Figure 4-4. Geology of the Lovisa area /Laitala 1964, Simonen and Laitala 1970, Laitakari and Simonen 1962, Simonen 1965/ with location of investigated samples.

5 Sampling and analytical methods

Samples from thin (< 10 mm), vertical-subvertical fluorite veins were collected from six sites in the Götemar area (Figure 4-2), ten sites in the Tindered area (Figure 4-3), and ten sites in the Lovisa area (Figure 4-4). All samples are listed in Table 5-1. The fluorite is found as thin coatings on fracture planes, which have become exposed when the road (or quarry) was constructed/exploited. Fluorite veins outside these artificial outcrops are very rare. The general appearance of the fluorite is quite similar in all three target areas, despite their wide geographical distribution. Most fluorites exhibit intergrown, well developed cubic crystal faces on the surface (center of fracture during formation). However, crystal size and colour varies, even within individual fracture planes in each area. Weak colour banding is only observed in one fracture at Tindered (see below). No field evidence argue against a contemporaneous formation of the fluorite veins within each of the three investigated areas.

Sample #	Locality	Site	Host rock	Analysis	Note
Kr 03-50	Götemar	Kråkemåla 2	Götemar granite	REE	Greisen-like
Kr 03-51	Götemar	Kråkemåla 2	Götemar granite	Sm-Nd	
Kr 03-53	Götemar	Kråkemåla 2	Götemar granite/ss dyke	Sm-Nd	
Kra 03-54	Götemar	Kråkemåla 1	Götemar granite	REE, Sm-Nd	
Kv 03-56	Götemar	SE of Kråkemåla	TIB granitoid, contact zone	REE, Sm-Nd	
Kv 03-57	Götemar	SE of Kråkemåla	TIB granitoid, contact zone	REE, Sm-Nd	
Ti 03-38	Tindered	Subarea 9	Biotite granite	REE, Sm-Nd	
Ti 03-39	Tindered	Subarea 5	Porphyritic granite	REE, Sm-Nd	
Ti 03-40	Tindered	Subarea 5	Porphyritic granite	REE	
Ti 03-41	Tindered	Subarea 7	Biotite granite	REE, Sm-Nd	
Ti 03-42	Tindered	Subarea 9	Biotite granite	REE	
Ti 03-43	Tindered	Subarea 5	Porphyritic granite	REE, Sm-Nd	
Ti 03-44	Tindered	Subarea 3	Porphyritic granite	REE	
Ti 03-45	Tindered	Subarea 2	Porphyritic granite	REE	
Ti 03-46	Tindered	Subarea 2	Porphyritic granite	REE	
Ti 03-47	Tindered	Subarea 1	Biotite granite	REE, Sm-Nd	
Me 03-01	Lovisa	Metsola	Pyterlite	REE	
Me 03-02	Lovisa	Metsola	Pyterlite	REE	
Me 03-03	Lovisa	Metsola	Pyterlite	REE, Sm-Nd	
Me 03-04	Lovisa	Metsola	Pyterlite	REE	
Me 03-05	Lovisa	Metsola	Pyterlite	REE	
Me 03-06	Lovisa	Metsola	Pyterlite	REE, Sm-Nd	
Me 03-07	Lovisa	Metsola	Pyterlite	REE, Sm-Nd	
Hv 03-08	Lovisa	Hästholmsvägen	Porphyry aplite	REE, Sm-Nd	
Hv 03-09	Lovisa	Hästholmsvägen	Porphyry aplite	REE, Sm-Nd	
Hv 03-10	Lovisa	Hästholmsvägen	Wiborgite	REE	

|--|

ss – sandstone dyke.

In the Götemar area, fluorite was collected in the abandoned Kråkemåla 2 quarry (Kr 03-50, Kr 03-51, Kr 03-53), in the active Kråkemåla 1 quarry (Kra 03-54), and in a road cut southeast of Kråkemåla 2 (Kv 03-56, Kv 03-57), see Figure 4-2. Of the three Kråkemåla 2 samples, # 50 was taken from a thin, very fine-grained, dark purple fluorite coating on a large dimension stone. Under the microscope, this fracture infilling proved to be greisenlike, consisting of extremely fine-grained fluorite, like a fine powder, and abundant white mica. This fluorite is considered not to be related to the Phanerozoic mineralizing event but more likely to a late magmatic stage of the Götemar intrusion. It is therefore not included in the isotope study. Sample # 51 was taken in a fracture, which crosscuts a sandstone dyke (close to field obs 89:18 in /Alm and Sundblad 2002/) and consists of mm-sized crystals of purple fluorite associated with calcite. Sample # 53 is from a fracture plane with a sandstone dyke and fluorite coating on the sandstone (field obs 89:16 in /Alm and Sundblad 2002/). The fluorite crystals are less than 1 mm in size, clear and colourless or purple. The Kråkemåla 1 sample consists of mm-sized purple fluorite grains associated with calcite. All Kråkemåla fluorites are hosted in coarse-grained Götemar granite. The two samples Ky 03-56 and Ky 03-57 are hosted in a fine-grained Småland granite, which is partly sheared near the contact to the Götemar granite. The fluorite in # 56 (from the same fracture plane as sample GM 01-15 in /Alm and Sundblad 2002/) and # 57 (some 70 m to the north) is yellow to colourless or pale purple, with up to 1 cm-sized crystals. Pyrite is common on the fracture where sample # 56 was collected.

The Tindered fluorites were sampled in subareas 1, 2, 3, 5, 7 and 9 in both types of granitic host rocks (Figure 4-3). The fluorite crystals are commonly up to 0.5 mm or rarely 10 mm in size. The colour varies from dark purple (one specific site in subarea 9; sample Ti 03-38) to semibanded bluegreen and pale purple (one specific site in subarea 5; sample Ti 03-44; same as Ti 01-18 in /Alm and Sundblad 2002/), pale purple, yellow or white/colourless. Calcite and galena are associated with this fluorite. Galena is also present in samples # 40, 41, and 45.

Of the ten Lovisa fluorites, seven were collected in road cuts located along circa one km of the main road east of Metsola (samples Me 03-01 to 03- 07), Figure 4-4. The colour of the fluorite is mostly yellow, white/colourless or to a lesser extent pale purple. The fluorite is fairly coarse-grained and crystals 0.5–1 cm in size are abundant. The host rock is a pyterlite. Three fluorites were sampled in two road cuts along Hästholmsvägen; samples Hv 03-08 and 03-09 in two outcrops on either side of the road c 3 km southeast of Lovisa, and Hv 03-10 c 450 m further to the southwest. The fluorite is similar at all sites; pale yellow or purple to white/colourless and up to 0.5 cm in size. The host rock to sample # 10 is a wiborgite, while # 08 and 09 are hosted in a porphyric aplite. It can be noted that no calcite or galena is found associated with the fluorite in the Lovisa area.

Fluorite was mechanically separated from adjacent wall rock fragments and 3–10 g of fluorite grains were handpicked in alcohol under microscope and ground in an agate mortar. Varying (but mostly small) amounts of included Fe-hydroxide, pyrite (marcasite?), or calcite could not be avoided in these separates. Four Götemar, ten Tindered, and ten Lovisa fluorite separates were analyzed for trace element contents using ICP-MS at Acme Analytical Laboratories LTD, Vancouver.

Five samples from each area were selected for the isotopic investigation, partly based on the results of the ICP analyses. Some 150 mg of purest possible fluorite grains were handpicked in alcohol under microscope. The fluorites were dissolved on hot plate in Savillex screw-cap Teflon beakers using HCl and H₃BO₃. Standard procedures /e.g. Hanski et al. 2001/ were used for chemical treatment and mass-spectrometry. Chemistry and isotope analyses were conducted at the Geological Survey of Finland, Espoo. Age calculations were performed using Isoplot/Ex rev 2.49 /Ludwig 2001/.

6 Results

The results of the REE analyses are plotted in Figures 6-1, 6-2 and 6-3, presenting chondrite-normalized /Boynton 1984/ REE profiles for the investigated fluorites.

For the Götemar area, REE data are available for four samples, of which only one is from a typical fluorite vein within the Götemar granite (Kra 03-54). The other three are the greisen-like fluorite (Kr 03-50) and the two fluorite samples collected immediately outside the Götemar granite (Kv 03-56, Kv 03-57). Two of the collected Götemar samples were too small to allow for geochemical analyses. Sample Kra 03-54 displays a slightly fractionated LREE distribution pattern, a pronounced negative Eu anomaly and fairly flat HREE with Lu enrichment relative to Yb (Figure 6-1). The REE pattern for the greisen-like sample (Kr 03-50) shows more fractionated LREE, a smaller Eu anomaly and depleted HREE compared to # 54. The REE patterns of samples # 56 and 57 are similar to each other but differ from that of # 54 through flat LREE, smaller Eu anomalies, and flat HREE that are enriched relative to the LREE.

Ten data sets are available for the REE contents in Tindered fluorites. Eight of these have fairly uniform REE patterns (Figure 6-2), with rather flat LREE curves, large negative Eu anomalies, and HREE that are constantly enriched relative to the LREE, although slightly decreasing from Er to Lu. Ti 03-41 has a similar pattern but generally with higher REE contents. Ti 03-44 (the only sample with green colour) is significantly more fractionated both in LREE and HREE.



Figure 6-1. REE patterns for the Götemar fluorites.



Figure 6-2. REE patterns for the Tindered fluorites.

All ten REE profiles for Lovisa fluorites are very similar, albeit with some variation in LREE fractionation (Figure 6-3). A weak distinction between the Metsola and Hästholmsvägen populations may be discerned. The latter (Hv 03-08 to 03-10) are slightly depleted in La relative to Ce, whereas the Metsola fluorites have flat LREE patterns or are enriched in La and Ce relative to Nd. For all samples, the negative Eu anomalies are large and HREE are enriched relative to the LREE but decreasing from Er to Lu (cf Tindered profiles, Figure 6-2).

According to the REE data, the Sm and Nd contents of fluorites in the Götemar, Tindered and Lovisa areas are fairly high and display a narrow range (4 to 10 ppm Sm, and 12 to 23 ppm Nd) for most samples. The only exceptions are samples Ti 03-41 and Ti 03-44 (Tindered), which have distinctly higher contents (Figure 6-2). The Sm/Nd ratios vary from 0.33 to 0.42 for the three non-greisen-like Götemar fluorites, from 0.36 to 0.65 for the Tindered fluorites, and from 0.39 to 0.56 for the Lovisa fluorites. To optimize the possibilities for well constrained isochrons, the samples for Sm-Nd isotope investigation were selected so that the largest spread in Sm/Nd ratios was obtained for each area.

All Sm-Nd isotope analyses are technically of a high quality and the results are presented in Table 6-1.



Figure 6-3. REE patterns for the Lovisa fluorites.

Sample	Location	Sm (ppm)	Nd (ppm)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	ε _{Nd} (400)
Me 03-03	Lovisa	8.51	16.67	0.309	0.512	-14.1
Me 03-06	Lovisa	7.83	20.05	0.236	0.512	-13.7
Me 03-07	Lovisa	7.28	13.39	0.329	0.512	-13.9
Hv 03-08	Lovisa	6.37	11.35	0.339	0.512	-13.8
Hv 03-09	Lovisa	5.59	9.78	0.346	0.512	-13.5
Ti 03-38	Tindered	7.72	19.05	0.245	0.512	-14.8
Ti 03-39	Tindered	5.92	10.84	0.330	0.512	-13.4
Ti 03-41	Tindered	33.76	51.96	0.393	0.512	-15.0
Ti 03-43	Tindered	6.46	13.63	0.287	0.512	-13.9
Ti 03-47	Tindered	6.97	18.18	0.232	0.512	-12.9
Kr 03-51	Götemar	9.16	25.62	0.216	0.512	-15.4
Kr 03-53	Götemar	1.76	7.83	0.136	0.512	-15.5
Kra 03-54	Götemar	6.23	19.22	0.196	0.512	-15.2
Kv 03-56	Götemar	5.88	13.44	0.264	0.512	-13.6
Kv 03-57	Götemar	9.79	20.56	0.288	0.512	-12.0

Table 6-1. Sm-Nd isotope data.

Error in $^{147}Sm/^{144}Nd$ is 0.4%, and in $^{143}Nd/^{144}Nd$ 0.00001 (absolute 2 σ error).

7 Discussion

The REE profiles of the investigated fluorite samples may, at least to some extent, reflect the REE distribution in the various host rocks to the fluorites. This is indicated by the significant negative Eu anomalies, particularly for the Lovisa and Tindered fluorites, which are typical for evolved or A-type granites like the Wiborg rapakivi granite and the differentiated granites at Tindered. At present, sufficient reliable REE data for the specific host rocks to the fluorites are not available, and therefore, a qualified comparison between the fluorite and host rock REE profiles cannot be made. The negative fractionation, with HREE enrichment relative to the LREE displayed in all investigated areas, may be due to variations in the complexing behaviour between LREE and HREE in the hydrothermal fluid, as suggested by, e.g. /Möller and Morteani 1983/.

The Sm-Nd isotope data are plotted in standard diagrams both for the entire population (Figure 7-1) and for all data in each individual area (Figures 7-2 to 7-4). It is evident that there is significant scatter of the data points and no proper isochrons are obtained. Therefore, the calculation results (Table 7-1) cannot be considered as true ages. The Lovisa population has the lowest MSWD value (6.6) and the calculated age estimate may hence be considered as a reasonable approximation, but the uncertainty is large and the absolute timing of fluorite formation is not constrained. When all fluorites are plotted in one diagram (Figure 7-1), it results in a reference line, corresponding to an age of 448 ± 62 Ma, but with a very large scatter (MSWD = 82) as can be expected from a population with such a heterogeneous source. Also the Götemar and Tindered data sets exhibit MSWD values far beyond the analytical error, which may be due to variations in initial Nd isotopic ratios of the source rocks in each area. The variation in initial Nd isotopic composition may also be due to contribution of different minerals or proportion of species, which actually are the source for Nd in fluorite. The question is whether such variation is possible even within a very homogeneous source rock, i.e. fluids with different compositions may have different dissolving power. A critical evaluation of each population is thus warranted.

Even if all fluorites from the Götemar area originally were considered to be generated by the Götemar pluton, the isotopic results clearly show that there is a significant inhomogeneity with respect to sources for the data involved in the calculation (Figure 7-2). It is therefore important to remember that two of the samples in the Götemar population (Kv 03-56 and Kv 03-57) were collected in veins immediately outside the Götemar pluton. Although the Götemar granite is still likely as the source for F, a contribution from other sources (TIB) cannot be excluded for Ca and REE in these two samples. A calculation using only the three samples from within the Götemar pluton, Kr 03-51, Kr 03-53 and Kr 03-54, yields an age of 414 ± 380 Ma (MSWD = 5.2), which better may reflect a single source. A similar age, 405 ± 27 Ma is obtained if only the two fluorites collected in the same quarry (Kr 03-51 and Kr 03-53) are combined (Figure 7-2).

Table 7-1. Calculation results of the Sm-Nd analytical data on fluorites representing the entire population of all three areas as well as each individual area.

Area	Age (Ma)	ε _{νd} (400 Ma)	MSWD	n
All three areas	448 ± 62	-14.4	82	15
Götemar	568 ± 180	-14.8	72	5
Tindered	355 ± 170	-13.3	81	5
Lovisa	406 ± 73	-13.8	6.6	5



Figure 7-1. Sm-Nd plot for fluorites, all three areas.



Figure 7-2. Sm-Nd plot for fluorites, Götemar.

Although two types of host rocks are identified in the Tindered area, the age calculations (Figure 7-3) cannot be improved by simple reorganizing of the isotope data with respect to host rock types. The reason for the large scatter among the Tindered fluorites thus remains unknown.

As can be seen in Figure 7-4, the five Lovisa samples plot on a reference line, which corresponds to a poorly constrained age of 406 ± 73 Ma. There are no obvious geological reasons to exclude any of the samples from the calculation, but the age estimate may be improved if Sm-Nd data for a realistic source rock are added. The Lovisa fluorites are hosted by various types of granites within the Wiborg batholith; the Metsola fluorites by pyterlites (although wiborgites occur only few hundred metres away from the investigated veins), and the Hästholmsvägen fluorites by porphyry aplites, very close to the wiborgites. One (or several) granite type(s) of the Wiborg batholith is thus the by far most probable source for the fluorite-forming fluids at Lovisa. The Sm-Nd isotopic composition of a representative sample of the Wiborg batholith might therefore be used to enhance the age calculation of the Lovisa fluorites, assuming that the selected Wiborg sample is adequate as a source of the investigated fluorites. For this purpose, analytical data generated by /Rämö 1991/ for a sample collected in the central part of the Wiborg batholith at Muurikkala, 90 km east of Lovisa, was used. The sample (A29b) is from a typical wiborgite with an age of $1,633 \pm 5$ Ma /Suominen 1991/. The Sm-Nd data for this sample is plotted together with the data generated for the Lovisa fluorites (Figure 7-5), and the combined data set yields an age of 401 ± 38 Ma (MSWD = 5.1).



Figure 7-3. Sm-Nd plot for fluorites, Tindered.



Figure 7-4. Sm-Nd plot for fluorites, Lovisa.



Figure 7-5. Sm-Nd plot for fluorites and one representative sample of a source rock, Lovisa.

The age obtained for the combined (fluorite and rock) set of data for the Lovisa fluorites is close to the age derived from the fluorite-only Lovisa population (406 ± 73 Ma) and may, with reservations, be regarded as an estimate of the age of the Lovisa fluorites. This age is in close agreement with the restricted Götemar fluorite population (405 ± 27 Ma, n = 2), see Figure 7-2. In Figure 7-6, these data are plotted together. They form two lines with the same slope but with different initial Nd isotopic ratios, as expected if they represent coeval fluorites derived from two geochemically different rocks. These age estimates are also comparable with that of all fluorites (448 ± 62 Ma). A revised summary of possible ages for fluorites from the three areas is presented in Table 7-2.

Table 7-2. Calculation results of the Sm-Nd analytical data on fluorites representing all three areas (entire population), Götemar (restricted populations), Tindered (entire population) and Lovisa (entire population and a realistic source rock).

Area	Age (Ma)	ε _{νd} (400 Ma)	MSWD	n
All three areas	448 ± 62	-14.4	82	15
Götemar	414 ± 380	-15.2	5.2	3
Götemar	405 ± 27	-15.4		2
Tindered	355 ± 170	-13.3	81	5
Lovisa	401 ± 38	-13.7	5.1	6



Figure 7-6. Sm-Nd plot for the combined data set of Lovisa (fluorites and a realistic source rock) and the restricted data set for Götemar, showing parallel lines with different initial Nd values.

In this way, possible ages of c 400 Ma are apparent for all three target areas, which is realistic from the perspective that geological, textural and lead isotopic arguments have indicated a Phanerozoic emplacement of the fluorites. 400 Ma is close to the border between Silurian and Devonian and represents one of the most dramatic periods in the Fennoscandian geological history, since it marks the culmination of the Caledonian orogeny /Stephens and Gee 1989/. At that time the Laurentian continent collided with Baltica, with subsequent nappe transport and uplift, followed by rapid erosion and redeposition of flysch-like sediments. This orogeny involved lateral stress phenomena related to the collision as well as vertical stresses induced from the overthrusting nappes and post-orogenic sedimentation. If the preliminary age estimate of 400 Ma is true for the investigated fluorites, it is obviously not difficult to find a relevant geodynamic framework for the processes that were responsible for the fracture systems and the Ca-, F- and Pb-bearing hydrothermal fluids.

Several independent reports have indicated large-scale reworking of the Precambrian crust in Palaeozoic time and lend support to such a timing of the fluorite formation. /Smellie and Stuckless 1985/ noted that U and Pb in the Götemar granite was mobilized in conjunction with hydrothermal activity, possibly at 420 ± 171 Ma, which fits excellently with a model involving formation of fluorite veins and radiogenic galena in Götemar at that time. A similar timing may be inferred for the vertical movement along the N-S-trending post-Cambrian fault in Götemar, documented by /Kresten and Chyssler 1976/. /Larson and Tullborg 1998/ paid attention to the fact that most U-Pb isochrons in the Swedish Precambrian have lower intercepts in the range 200-400 Ma and concluded that this is due to pressure-induced reworking of the Precambrian crust in conjunction with increased thicknesses of Palaeozoic sedimentary cover rocks. Furthermore, c 450 Ma low-temperature mobilization of uranium near the sub-Cambrian peneplane in eastern Uusimaa, southern Finland, has been suggested based on U-Pb ages of uraninites /Vaasjoki et al. 2002/. All this may indicate that the preliminary ages of c 400 Ma of the fluorite veins reflect significant mobilization of several elements in the Precambrian crust of the entire Fennoscandian Shield. It should, however, be remembered that the fluorite ages presented in Table 7-2 still are preliminary and any further speculation on this theme is premature until the ages are better constrained.

The calculation results of combined data sets from fluorites and a realistic source rock (the A29b sample of the Wiborg batholith) are so promising that such combined data sets should be generated also for the Tindered and Götemar systems as well as for the rapakivi rocks close to the Lovisa veins. It is therefore strongly suggested that the project is allowed to continue the evaluation of the Sm-Nd systematics of the fluorite veins and in their presumed source rocks. The following steps are suggested in such a continuation project:

- Proper mapping of the vein systems and their host rocks in the Lovisa region, so as to arrive at the same level of knowledge as already has been achieved for Götemar and Tindered.
- Obtain Sm-Nd data on the possible source rocks in all three areas.
- Obtain REE data on the possible source rocks in all three areas.

8 Conclusions

Sm-Nd isotope analyses of Phanerozoic fluorites from three target areas (Götemar and Tindered in Sweden, and Lovisa in Finland) result in linear trends with such high MSWD values that they do not define any proper isochrons. The line obtained for the Lovisa fluorites has the lowest MSWD value (6.6) and might be considered as a poorly defined isochron with an age of 406 ± 73 Ma. This age estimate can be improved by adding Sm-Nd data for a possible source rock to the fluorite data, which results in an age of 401 ± 38 Ma and a MSWD value of 5.1. If the two TIB-hosted samples are excluded from the Götemar population, an age of 414 ± 380 Ma (MSWD = 5.2) is obtained. A similar age of 405 ± 27 Ma is obtained by combining the two spatially most closely related samples in the Götemar population. The Sm-Nd data for the Tindered area yields an age of 355 ± 170 Ma, but with a large scatter indicating sources with variation in initial Nd isotopic ratios. More or less clear indications for ages of c 400 Ma are thus obtained for the fluorite systems in all three target areas. This is geologically realistic and fits with models for Palaeozoic low-temperature mobilization of U and Pb that have been proposed by other workers. Further work is, however, needed if better constraints for these age estimates should be obtained. It is particularly recommended that the Sm-Nd isotope systematics of the host rocks are investigated in order to provide reliable isochrons.

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