Fluorine in orthoamphibole dominated Zn–Cu–Pb deposits: examples from Finland and Australia

LEENA RAJAVUORI[1] & LEO M. KRIEGSMAN[1,2]
[1]*Department of Geology, University of Turku, 20014 Turku, Finland*
[2]*National Museum of Natural History, PO Box 9517, 2300 RA Leiden, the Netherlands*
(e-mail: kriegsman@naturalis.nnm.nl)

Abstract: Volcanogenic massive sulphide (VMS) deposits commonly occur within much larger fluorine (F)-bearing hydrothermal systems, where cordierite–orthoamphibole rocks are characteristic pathfinder assemblages. Here we report whole-rock and mineral F contents for orthoamphibole bearing rocks and associated rock types from Zn–Cu–Pb deposits in Finland (Orijärvi, Iilijärvi, Pyhäsalmi, Mullikkoräme) and central Australia (Oonagalabi). Textural and mineralogical data suggest that F influx predates peak metamorphism in these deposits.

The Mullikkoräme whole-rock data show positive correlations between F and X_{Mg} = molar Mg/(Mg + Fe) and between F and elements of relatively low mobility (Ti, Al, Mg) and negative correlations between Fe and these elements. This suggests that iron was leached from silicate rocks by F-bearing fluids and was transferred to the Fe-rich sulphide ore. When normalized to immobile elements, F correlates positively with total metal content (Cu + Pb + Zn + Fe), consistent with the commonly observed increase of F content towards ore bodies.

Combining all microprobe data, hydrous minerals show the following order of decreasing F/(F + OH) ratio when coexisting: apatite > chondrodite > biotite > gedrite > (hornblende, muscovite, anthophyllite) > chlorite. The low- to medium-grade Finnish samples (Mullikkoräme: 500–560 °C at 1–3 kbar; Orijärvi: 550–650 °C at 3–5 kbar; Pyhäsalmi: 600–700 °C at 5–7 kbar) contain mainly F-poor anthophyllite, whereas F-rich gedrite is dominant in the higher grade Oonagalabi deposit (750–800 °C, 8–9 kbar). Temperature seems to have a significant, but X_{Mg} a negligible influence on F partitioning between biotite and orthoamphiboles.

Fluid–rock interaction has become one of the main issues addressed by metamorphic geologists over the past few years. In order to evaluate the potential of crustal fluids in transporting and concentrating elements in different types of ore deposits, it is critical to constrain their composition and source. Mineral chemical equilibria (e.g., papers in Humphris *et al.* 1995; Wood & Samson 1998), fluid inclusion and stable isotope studies (e.g, Heaton & Sheppard 1977; Barnes 1979) have been widely applied for this purpose. An alternative approach uses the capability of high-grade minerals to act as a sink for fluids in crustal rocks and hence to act as a monitor of fluid–rock interaction.

Magmatic volatiles, such as H_2O, F, Cl and Br, play a crucial role in magmatic–hydrothermal ore formation, and F (as well as Cl) can transport metals as aqueous metal halide complexes. Many volcanogenic massive sulphide (VMS) deposits occur in F-bearing hydrothermal systems, which are usually more voluminous than these ore deposits and therefore more easily recognizable (Lavery 1985). Hence, a geochemical exploration strategy is to use F as a pathfinder element to trace hydrothermal systems and then to locate possible ore deposits within the system. The average F content in volcanic rocks is usually below 500 ppm; in F-enriched rocks it can easily rise to several thousand ppm. Anomalous F values often define a distinctive zone stratigraphically above and below the sulphide ores, and F contents are usually highest near ore bodies (Lavery 1985).

Available studies on the behaviour and distribution of F in natural rocks and fluids suggest that (i) F is strongly partitioned into the solid phases during fluid–rock interaction (Anfilogov *et al.* 1977; Willner *et al.* 1990; Zhu & Sverjensky 1991; Willner 1993); (ii) F stabilizes relict biotite and amphiboles during high-grade metamorphism and partial melting (Foley 1991; Peterson *et al.* 1991; Hensen & Osanai 1994; Tareen *et al.* 1995; Dooley & Patiño-Douce 1996); (iii) high F contents are common in A-type granites (Collins *et al.* 1982; Kovalenko & Kovalenko 1984; Rogers & Satterfield 1994; Hogan & Gilbert 1997); and

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(iv) high F contents are common in rocks associated with massive sulphide deposits (Lavery 1985; Jiang *et al.* 1994) and Au deposits (Matthäi *et al.* 1995). Hence, it seems that pre-metamorphic F may persist in high-grade metamorphic rocks. If metamorphism is unrelated to F influx, this could allow one to 'see through' the various metamorphic events and investigate the role of F in the mineralizing fluids during earlier hydrothermal processes.

Orthoamphibole–cordierite rocks are rare, but characteristic rock types that have been studied intensely ever since the first detailed petrographical descriptions of the Orijärvi outcrops in Finland (Eskola 1914, 1915). Many of these rocks are associated with sulphide ore deposits (Eskola 1914; Froese 1969; Zaleski & Peterson 1995; Treloar *et al.* 1981; Wolter & Seifert 1984; Moore & Waters 1990; Dobbe 1994; Pan & Fleet 1995), which partly explains the interest in these possible pathfinder assemblages. Alteration suites around ore deposits often exhibit vertical and lateral zonation, which is expressed as sericification, silicification, chloritization and a cordierite–orthoamphibole association (Vallance 1967; Sánchez-España *et al.* 2000). The stabilizing effect of F in orthoamphiboles is, however, not yet well documented. In addition, orthoamphibole–cordierite rocks have a high potential for the study of phase relations and the derivation of the medium- to high-grade segments of *P–T* paths (Robinson *et al.* 1981; Schumacher & Robinson 1987; Visser & Senior 1990; Schneiderman & Tracy 1991). Orthoamphibole–cordierite-bearing rocks show a different mineralogy at higher *P–T* conditions. In transitional granulites, orthoamphibole may coexist with orthopyroxene and cordierite (West Uusimaa, Finland: Schreurs & Westra 1985); with orthopyroxene and garnet (altered felsic rocks in Oonagalabi, central Australia: Raith & Kriegsman 1998) or with spinel, corundum, chondrodite and sapphirine (same area, altered mafic to ultramafic rocks). The high-pressure, high-temperature Oonagalabi rocks occur in an orthoamphibole-dominated unit, which hosts a small, presently sub-economic, Cu–Zn–Pb deposit (Stewart & Warren 1977), underscoring the similarity with low-pressure, medium-temperature orthoamphibole–cordierite rocks.

The present study uses whole-rock and mineral chemistry to assess the role of F in (i) hydrothermal activity leading to strongly altered felsic and mafic sequences and associated sulphide ore deposits and (ii) medium- to high-temperature metamorphism producing orthoamphibole bearing assemblages. The emphasis is on samples from Finland (Orijärvi, Iilijärvi, Pyhäsalmi, Mullikkoräme), but samples from Oonagalabi are used to provide additional constraints on F partitioning data between hydrous phases.

Methods employed

Whole-rock analyses were made on 20 selected samples from Orijärvi, which were crushed and powdered at the Department of Geology, University of Turku. Powders were analysed at Genalysis Laboratory Services Ltd., Perth, Australia. ICP-AES techniques were used for Na, Ca, Mn, P, Zn, Cr, Ni, Cu and V (acid digest) and for K, Fe, Mg, Al, Ti, S and B (peroxide fusion). ICP-MS techniques were used for REE, Ba, Rb, Sr, Th, Y, U, Pb, As, Te, Be and W (acid digest) and for Nb, Ta, Zr and Hf (peroxide fusion). F and LOI (loss on ignition) were also measured except for sample LMR 49. For F extraction, the sample was fused with a flux of sodium carbonate, potassium carbonate, zinc oxide and silicic acid. The melt was then leached with water to dissolve the fluoride. International standards were fused with each set of samples and a calibration curve plotted each time the measuring electrode was used.

Whole-rock F contents varied from 150 to 3550 ppm (detection limit: 50 ppm; average: 979 ppm). SiO_2 was not analysed for Orijärvi samples, so their SiO_2 content was calculated by subtracting other element concentrations from 100% (Table 1). Existing geochemical databases (>1000 whole-rock analyses, 52 of which include F) on the Iilijärvi, Pyhäsalmi and Mullikkoräme deposits in central Finland, kindly provided by Outokumpu Mining Ltd, were used as additional sources of information and were critical for improving the statistical relevance of observed correlations. Some representative analyses are also given in Table 1. The total weight of some Mullikkoräme samples exceeds 100% because a considerable amount of Fe is in sulphide rather than oxide form (see geochemistry section). The total weight has also been corrected for oxygen in baryte and CO_2 (Table 1).

After petrological analysis (recognition of minerals in thin sections, assessment of their growth relationships and relative timing; qualitative evaluation of *P–T* conditions and possible *P–T* paths), minerals from polished thin sections of selected samples were analysed for major elements and F, using the JEOL JXA 8600 electron microprobe at the Department of Earth Sciences, University of Bristol. The detection limit for F is routinely put at 1000 ppm (= 0.1 wt%) but, with special care, analyses down to 50–100 ppm give reproducible results. Representative results are given in Tables 2 and 3.

Table 1. *Representative whole-rock analyses, including fluorine, from samples of the Orijärvi and Mullikkoräme deposits*

Area	ORI	ORI	ORI	ORI	ORI	ORI	MUL	MUL	MUL	MUL	MUL	MUL	MUL	MUL	MUL	MUL
Sample	LMR 7	LMR 34c	LMR 42	LMR 45	LMR 40a	LMR 54	MUR-273	MUR-144	MUR-273	MUR-144	MUR-293	MUR-314	MUR-293	MUR-144	MUR-283	MUR-326
Rock type	Grt–Bt gness	Crd–Ath rock	Crd–Bt gneiss	Mafic volcanite	Granodiorite	Felsic vulcanite	Mafic vulcanite	Felsic vulcanite	Skarn	Tlc skarn	Tlc–Chl skarn	Phl–Chl gneiss	Plg–Uralite porphyrite	Sphalerite–galena ore	Pyrite ore	Pyrite ore
SiO_2	56.54	64.90	60.61	52.69	72.58	73.35	37.90	61.50	32.60	30.00	43.10	53.50	40.80	17.80	7.95	18.30
TiO_2	1.5	0.33	0.72	0.7	0.3	0.2	0.42	0.33	0.20	0.06	0.06	0.28	0.02	0.02	0.02	0.01
Al_2O_3	14.74	12.09	16.25	15.87	13.6	12.09	8.78	11.60	9.14	2.60	2.86	11.00	1.24	1.15	0.91	0.86
FeO	11.58	7.72	6.43	9.78	2.44	3.15	21.90	6.41	16.56	21.60	12.96	13.86	15.57	14.31	15.48	29.69
MnO	0.1	0.14	0.05	0.17	0.05	0.04	0.65	0.07	0.14	0.14	0.204	0.10	0.061	0.252	0.209	0.171
MgO	5.31	11.61	5.47	8.95	0.9	0.93	17.20	4.35	11.60	22.70	23.5	7.46	22.6	21.4	11	13.4
CaO	2.17	0.17	2.1	6.58	2.8	1.75	1.56	3.24	7.62	1.28	4.65	1.54	1.39	4.54	18.9	4.23
Na_2O	2.7	0.16	2.97	3.57	4.58	3.98	0.10	0.73	0.85	–	–	1.41	–	–	–	0.24
K_2O	3.49	1.04	3.98	0.51	1.87	2.59	2.65	0.89	1.35	–	0.017	1.72	0.104	0.007	0.018	0.004
P_2O_5	0.46	0.05	0.12	0.09	0.07	0.03	0.09	0.10	0.18	0.107	0.123	0.09	0.079	0.044	0.34	0.165
LOI	0.88	1.46	0.85	0.89	0.58	1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
F	1000	2450	3550	300	650	150	4200	1000	2800	3400	4700	1300	4400	3500	900	1400
Cl	–	–	–	–	–	–	180	–	90	–	–	100	–	160	–	–
C	–	–	–	–	–	–	100	200	200	200	700	100	100	1700	55100	3900
S	2700	100	0	500	500	7200	58600	45300	124000	177000	85600	81900	117000	167000	136000	227000
Zn	125	265	62	125	27	68	22919	26304	23465	71354	49307	12053	75158	223330	98474	96970
Pb	12	42	8	32	8	14	–	11268	4631	1292	3300	533	9872	22677	3733	7525
Cu	15	19	2	50	4	37	6986	12289	2390	1348	2132	641	1322	215	5743	34186
Ni	0	2	4	64	3	3	–	–	–	–	–	21	–	23	–	49
Cr	70	130	80	280	160	108	–	–	–	–	–	–	–	–	–	–
V	155	24	114	220	14	0	101	–	–	–	–	–	–	–	–	–
Ba	920	64	330	94	490	900	5158	13414	5804	20	210	4492	120	177	6956	21
Rb	64	21.5	92	9.6	42	36	56	31	42	–	–	27	16	25	–	–
Sr	106	7.4	58	235	140	74	22	369	231	–	17	78	14	59	117	–
Y	13.5	8.6	9	12.5	27	21.5	15	29	19	–	–	20	–	–	–	–
Zr	72	112	94	42	145	165	100	203	106	31	29	147	12	14	15	–
Nb	7.5	11.5	7.5	3.5	12	13	–	19	10	–	–	–	–	–	–	–
Ce	38	40	54	17	64	56	76	200	78	–	–	92	–	–	–	–
Th	4	6	6.6	2.2	8.2	9	–	49	–	–	–	–	37	81	–	–
U	2.1	2.2	2.1	1.0	3.1	4.1	–	–	11	14	14	–	–	13	20	13
Total*	100	100	100	100	100	100	101.09	100.28	96.63	103.94	102.07	101.10	102.66	101.41	85.53	104.18
*Orijärvi samples: SiO_2 calculated as 100 – total of other elements																
wt% Fe in sulphides (calculated)							4.02	2.40	9.62	12.35	5.30	6.52	6.84	4.70	7.45	15.53
Real FeO (wt%)							17.43	3.32	4.19	5.71	6.14	5.47	6.76	8.27	5.90	9.72
Oxygen in baryte and CO_2							0.27	0.68	0.32	0.05	0.20	0.24	0.03	0.46	15.02	1.04
Total corrected for Fe in sulphides and oxygen in baryte and CO_2							100.91	100.27	94.20	100.45	100.75	99.47	100.74	100.53	98.42	100.77

Table 2. *Representative microprobe analyses and recalculated mineral formulae of amphiboles*

Area	ORI	IIL	IIL	IIL	OONA	ORI	IIL	ORI	OONA	OONA	OONA	OONA	OONA	OONA	OONA	OONA	IIL
Sample	62b	214	266	219	AR227b	62b	214	62b	AR126a	AR126a	AR126b	AR126c	AR126d	AR129	AR131b	AR245a	266
Mineral	Ath	Ath	Ath	Ath	Ath	Oam	Oam	Ged	Ged	Ged	Ged	Ged	Ged	Ged	Ged	Ged	Cum
ID	65	178	435	527	767	51	183	55	716	216	38	94	444	18	178	198	439
SiO_2	51.65	50.71	51.22	53.36	55.03	50.09	50.70	42.90	45.15	45.15	43.25	43.62	45.00	45.01	45.25	49.08	51.46
Al_2O_3	2.23	3.00	2.48	1.76	1.53	4.04	4.18	14.01	16.92	16.92	18.64	19.07	17.25	13.45	14.82	9.61	1.48
TiO_2	0.02	0.05	0.09	0.02	0.03	0.03	0.14	0.18	0.12	0.12	0.32	0.16	0.15	0.29	0.08	0.02	0.00
FeO	26.97	24.63	23.69	21.61	18.72	26.25	25.29	26.38	7.69	7.69	8.51	10.87	7.66	17.80	13.79	14.81	23.47
MnO	0.87	1.18	1.01	0.87	0.14	0.92	1.15	0.97	0.26	0.26	0.71	0.42	0.30	0.16	0.23	0.25	0.98
MgO	14.88	15.47	15.74	18.37	21.55	14.43	14.70	10.67	24.74	24.74	23.00	21.68	24.85	17.77	21.41	22.05	15.39
CaO	0.15	0.16	0.23	0.23	0.25	0.19	0.25	0.44	0.45	0.45	0.73	0.29	0.43	0.06	0.11	0.08	1.07
Na_2O	0.15	0.17	0.23	0.00	0.04	0.43	0.40	1.33	2.18	2.18	2.46	2.40	2.31	1.59	1.94	1.56	0.06
K_2O	0.01	0.03	0.01	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.02	0.02	0.01	0.00	0.01	0.01	0.02
ZnO	–	–	0.27	0.61	–	–	–	–	–	–	–	–	–	–	–	–	0.13
Cl	0.001	0.000	0.000	0.002	0.014	0.006	0.000	0.000	0.014	0.010	0.011	0.017	0.000	0.003	0.020	0.017	0.005
F	0.077	0.036	0.025	0.088	0.000	0.049	0.044	0.107	0.625	0.620	0.218	0.272	0.765	0.217	0.579	0.653	0.034
Total wt.	97.00	95.43	95.01	96.91	97.33	96.45	96.85	96.99	98.15	98.14	97.88	98.81	98.73	96.35	98.23	98.14	94.10
−O≡F,Cl	−0.03	−0.02	−0.01	−0.04	0.00	−0.02	−0.02	−0.05	−0.26	−0.26	−0.09	−0.11	−0.32	−0.09	−0.24	−0.28	−0.01
H_2O+ (calc.)	1.96	1.96	1.97	2.00	2.10	1.96	1.98	1.92	1.87	1.87	2.05	2.03	1.82	1.95	1.84	1.80	1.94
−FeO≡ Fe_2O_3	0.04	0.04	0.00	0.00	0.00	0.02	0.00	0.03	0.24	0.24	0.23	0.11	0.25	0.01	0.24	0.06	0.00
Corr. wt	98.97	97.42	96.96	98.88	99.42	98.41	98.81	98.90	100.00	100.00	100.06	100.84	100.47	98.22	100.06	99.73	96.03
Cations / 23 oxygens (total cations = 15+Na+K)																	
Si	7.753	7.675	7.762	7.829	7.859	7.564	7.587	6.513	6.203	6.202	5.993	6.043	6.159	6.577	6.372	6.947	7.878
AlIV	0.247	0.325	0.238	0.171	0.141	0.436	0.413	1.487	1.797	1.798	2.007	1.957	1.841	1.423	1.628	1.053	0.122
AlVI	0.147	0.210	0.205	0.134	0.117	0.284	0.325	1.020	0.942	0.942	1.037	1.156	0.941	0.893	0.831	0.550	0.145
Fe^{3+}	0.050	0.048	0.000	0.000	0.002	0.019	0.000	0.036	0.249	0.250	0.237	0.118	0.255	0.015	0.249	0.066	0.000
Ti	0.003	0.005	0.010	0.002	0.004	0.004	0.016	0.020	0.012	0.012	0.034	0.017	0.015	0.031	0.008	0.002	0.000
Mg	3.330	3.490	3.554	4.019	4.589	3.248	3.278	2.415	5.065	5.066	4.751	4.476	5.070	3.871	4.494	4.653	3.511
Fe^{2+}	3.336	3.069	3.003	2.652	2.234	3.297	3.165	3.313	0.634	0.633	0.749	1.141	0.621	2.160	1.375	1.687	3.004
Mn	0.110	0.151	0.130	0.108	0.016	0.117	0.145	0.125	0.030	0.030	0.084	0.049	0.034	0.019	0.027	0.030	0.127
Ca	0.024	0.026	0.038	0.036	0.039	0.031	0.040	0.072	0.067	0.066	0.109	0.043	0.063	0.010	0.016	0.012	0.176
Na	0.042	0.051	0.067	0.000	0.012	0.125	0.117	0.391	0.580	0.581	0.662	0.645	0.613	0.451	0.530	0.430	0.018
K	0.002	0.005	0.002	0.000	0.003	0.001	0.000	0.000	0.000	0.000	0.004	0.004	0.002	0.001	0.002	0.003	0.004
Zn	0.000	0.000	0.031	0.066	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.015
Cl	0.000	0.000	0.000	0.001	0.003	0.001	0.000	0.000	0.003	0.002	0.002	0.004	0.000	0.001	0.005	0.004	0.001
F	0.036	0.017	0.012	0.041	0.000	0.024	0.021	0.051	0.271	0.269	0.095	0.119	0.331	0.100	0.258	0.292	0.016
X_F	0.018	0.009	0.006	0.020	0.000	0.012	0.010	0.026	0.136	0.135	0.048	0.060	0.167	0.050	0.130	0.146	0.008
X_{Mg}	0.496	0.528	0.542	0.602	0.672	0.495	0.509	0.419	0.852	0.851	0.828	0.780	0.853	0.640	0.735	0.726	0.539

Table 3. *Representative microprobe analyses and recalculated mineral formulae of sheet silicates*

Place	IIL	IIL	IIL	ORI	OONA	OONA	OONA	OONA	OONA	OONA	OONA	OONA	ORI	MUR	ORI	ORI
Sample	214	219	266	62b	AR126a	AR126b	AR126c	AR126d	AR129	AR131b	AR245a	AR227b	55	142	62b	62b
Mineral	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Bt	Musc	Musc	Chl incl.	Chl
ID	179	509	445	73	240	46	101	371	22	170	204	287	7	334	87	59
SiO_2	36.79	38.94	35.88	37.14	42.50	40.42	39.67	42.22	38.78	40.73	39.97	37.64	45.32	44.81	24.89	24.45
Al_2O_3	17.02	16.12	17.53	18.17	13.67	15.86	16.84	13.82	15.40	14.39	14.49	15.97	28.20	35.58	21.93	21.66
TiO_2	1.51	0.98	1.61	1.20	0.52	1.13	1.15	0.41	2.13	0.72	0.64	3.45	0.68	0.08	0.07	0.08
FeO	17.73	12.34	15.58	17.30	2.32	3.77	5.33	2.29	7.97	5.53	5.10	10.45	4.66	1.14	22.47	23.04
MnO	0.10	0.07	0.16	0.02	0.02	0.04	0.04	0.02	0.02	0.02	0.04	0.01	0.15	0.00	0.19	0.24
MgO	12.58	16.71	12.58	13.07	26.19	24.49	22.66	26.93	20.13	23.80	24.02	17.42	4.67	0.37	15.97	15.95
CaO	0.00	0.00	0.10	0.01	0.02	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.07	0.03	0.02	0.01
Na_2O	0.35	0.33	0.29	0.25	1.04	0.71	0.73	1.12	0.75	0.53	1.11	0.23	0.11	0.74	0.03	0.00
K_2O	8.79	9.23	9.51	8.49	8.63	8.88	9.19	8.61	8.49	9.33	8.44	8.84	10.66	11.10	0.00	0.02
ZnO	—	0.16	0.18	0.00	–	–	–	–	–	–	–	–	–	–	0.00	0.00
Cl	0.00	0.01	0.00	0.01	0.02	0.02	0.04	0.03	0.03	0.12	0.12	0.02	0.004	0.005	0.000	0.002
F	0.24	0.63	0.13	0.20	1.76	0.87	0.75	1.90	0.90	1.66	1.63	0.11	0.053	0.049	0.034	0.006
Total wt.	95.11	95.54	93.55	95.87	96.68	96.20	96.39	97.36	94.61	96.81	95.55	94.13	94.58	93.90	85.61	85.46
−O=F,Cl	−0.10	−0.27	−0.06	−0.08	−0.74	−0.37	−0.31	−0.80	−0.38	−0.70	−0.69	−0.04	−0.02	−0.02	−0.01	−-0.00
H_2O+ (calc.)	3.86	3.77	3.85	3.93	3.45	3.85	3.88	3.40	3.68	3.40	3.37	4.01	4.32	4.39	11.25	11.18
$-FeO=Fe_2O_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.52	0.13	–	0.02
Corr. wt.	98.86	99.04	97.35	99.72	99.39	99.69	99.96	99.96	97.91	99.51	98.24	98.10	99.40	98.40	96.84	96.65
Nr. of oxygens	22	22	22	22	22	22	22	22	22	22	22	22	22	22	28	28
Si	5.561	5.732	5.494	5.526	5.938	5.678	5.606	5.873	5.657	5.798	5.745	5.547	6.176	6.069	5.302	5.241
Al IV	2.439	2.268	2.506	2.474	2.062	2.322	2.394	2.127	2.343	2.202	2.255	2.453	1.824	1.931	2.698	2.759
Al VI	0.592	0.529	0.658	0.713	0.188	0.302	0.412	0.139	0.305	0.212	0.199	0.320	2.706	3.748	2.807	2.712
Fe^{3+}	—	—	—	—	—	—	—	—	—	—	—	—	0.531	0.129	—	0.024
Ti	0.172	0.108	0.185	0.135	0.054	0.120	0.122	0.043	0.234	0.077	0.069	0.383	0.069	0.008	0.011	0.014
Mg	2.834	3.666	2.871	2.900	5.454	5.128	4.773	5.583	4.376	5.049	5.146	3.827	0.949	0.075	5.070	5.094
Fe^{2+}	2.242	1.520	1.995	2.153	0.272	0.443	0.630	0.267	0.972	0.658	0.613	1.288	0.000	0.000	4.002	4.106
Mn	0.013	0.009	0.021	0.002	0.003	0.005	0.005	0.003	0.003	0.002	0.004	0.001	0.017	0.000	0.035	0.044
Ca	0.000	0.000	0.017	0.002	0.002	0.000	0.000	0.001	0.002	0.000	0.000	0.000	0.010	0.004	0.004	0.003
Na	0.103	0.093	0.087	0.072	0.281	0.194	0.199	0.302	0.211	0.145	0.310	0.066	0.030	0.195	0.013	0.000
K	1.696	1.733	1.857	1.611	1.538	1.591	1.656	1.529	1.580	1.694	1.548	1.663	1.854	1.917	0.000	0.004
Zn	0.000	0.018	0.020	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cl	0.000	0.004	0.001	0.002	0.005	0.005	0.010	0.007	0.006	0.028	0.028	0.004	0.001	0.001	0.000	0.001
F	0.113	0.295	0.064	0.094	0.777	0.389	0.334	0.835	0.415	0.747	0.741	0.049	0.023	0.021	0.023	0.004
Total cations	15.651	15.675	15.711	15.587	15.792	15.783	15.797	15.866	15.681	15.838	15.888	15.548	14.166	14.075	19.941	20.000
X_F	0.028	0.074	0.016	0.023	0.194	0.097	0.083	0.209	0.104	0.187	0.185	0.012	0.006	0.005	0.001	0.000
X_{Mg}	0.558	0.707	0.590	0.574	0.953	0.921	0.883	0.954	0.818	0.885	0.894	0.748	0.641	0.369	0.559	0.552

Orijärvi area, southern Finland

Regional background

The Orijärvi area is located within the Svecofennian orogenic belt of SW Finland (Figs 1 and 2). The bedrock of the area is composed of supracrustal and infracrustal rocks that are of Palaeoproterozoic age (Mäkelä 1989). During the Svecofennian orogeny, the supracrustal rocks were deformed during a main foliation-forming event (D_1) and a subsequent refolding event (D_2), regionally metamorphosed and intruded by granodiorites (Schneiderman & Tracy 1991). Metamorphism in the area started during the early stages of the Svecofennian orogeny (1900–1870 Ma: Neuvonen *et al.* 1981) and reached peak temperatures (550–650 °C at 3–5 kbar: Schreurs & Westra 1985) at about 1830 Ma (Ploegsma & Westra 1990). After cooling, some shear zones were reactivated during the last deformation event at about 1530 Ma (Ploegsma & Westra 1990).

The Orijärvi area belongs to a metallogenic zone that extends from the southwestern part of Finland to central Sweden. There are several principal ore deposits in the Finnish section of that zone: the Aijala Cu–Zn deposit (Mäkelä 1983), the Metsämonttu and Attu Zn–Pb deposits, the Orijärvi Cu–Zn deposit (Latvalahti 1979) and the Iilijärvi Zn–Pb–Ag(–Au) deposit located 1.3 km northwest from the Orijärvi mine. The Orijärvi and Iilijärvi deposits lie within the same zone (Fig. 2) of altered rocks. The zone is composed of several elongated lenses of cordierite–anthophyllite rocks; these lenses are tens to hundreds of metres in length and less than 300 m in width. The ores and their host rocks are intensively deformed and metamorphosed (Colley & Westra 1987). The Orijärvi deposit is located within a zone that is composed of andalusite–cordierite–muscovite gneisses, cordierite–muscovite–biotite gneisses with garnet porphyroblasts and cordierite–anthophyllite gneisses. Mineral deposits are associated with strongly hydrothermally altered rocks (Eskola 1914; Latvalahti 1979) that occur in two separate zones (Mäkelä 1989). The Zn–Pb–Cu ore in the main ore zone occurs in narrow, elongated bodies. It is hosted in a diopside–tremolite skarn. Common ore minerals are pyrite, chalcopyrite, sphalerite and galena (Mäkelä 1989; Colley & Westra 1987; Papunen 1986). The Cu–Zn ore lies 50 m south of the main zone and is hosted in cordierite–anthophyllite rocks. Common ore minerals in this ore deposit are sphalerite, pyrrhotite, chalcopyrite and galena (Mäkelä 1989; Colley & Westra 1987; Papunen 1986).

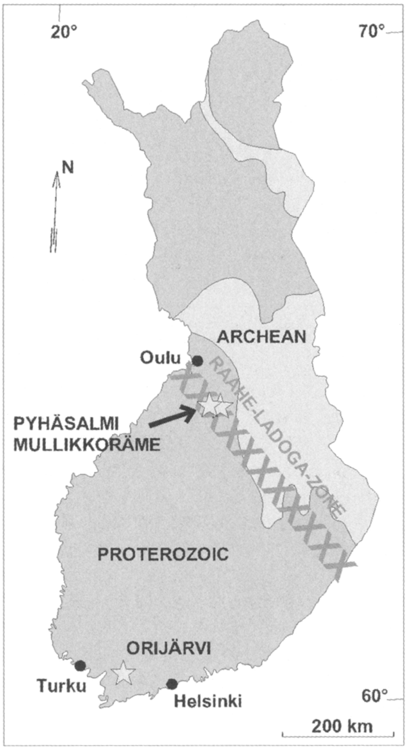

Fig. 1. General geological map of Finland, showing the locations of the Orijärvi, Pyhäsalmi and Mullikkoräme Zn–Cu–Pb deposits

Petrography

Petrographic studies indicate that quartz, plagioclase, zircon, titanite, fluorite, apatite and opaque minerals usually predate D_1 deformation whereas phlogopite, gedrite, anthophyllite, cordierite and cummingtonite crystallized pre- to syn-kinematically with respect to a first deformation phase (D_1). Peak temperatures (550–650 °C) in the Orijärvi area were reached syn- to post-kinematically with respect to a second deformation event (D_2) and garnets, often associated with cummingtonite, have probably grown at that stage (Bleeker & Westra 1987). In many places, amphiboles have recrystallized at this stage and have coarsened and randomly overgrown earlier, well-aligned amphiboles.

Fluorite is a common accessory mineral in most rock types in the Orijärvi area with the exception of the amphibolites and granodiorites. As fluorite and F-rich apatite commonly form inclusions in porphyroblastic minerals (cordierite, anthophyllite, garnet), they must have crystallized before peak metamorphism. This suggests that F-bearing fluids entered relatively early into the system, consistent

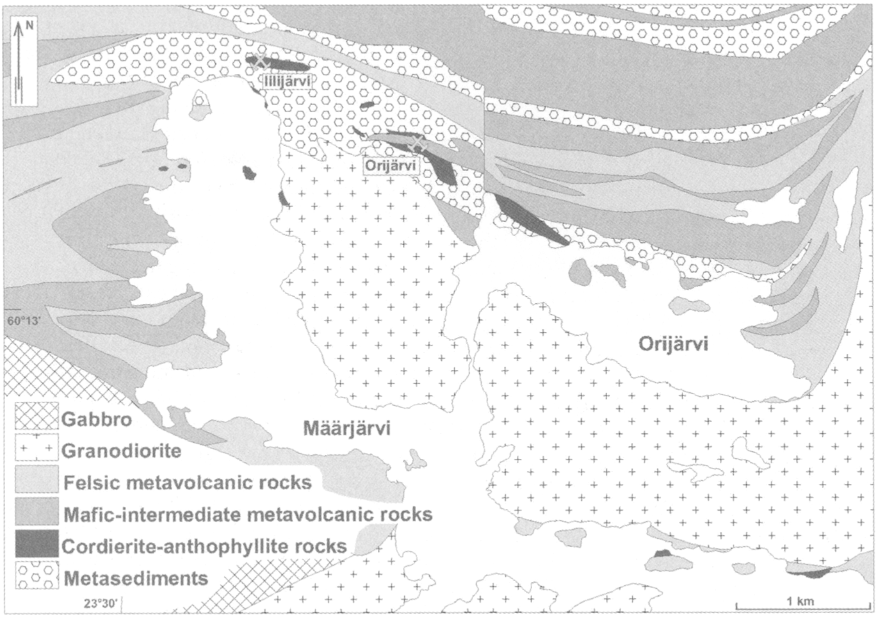

Fig. 2. Geological sketch map of the Orijärvi area (after data kindly provided by M. Väisänen)

with conclusions of earlier workers (Eskola 1914; Latvalahti 1979; Mäkelä 1983).

Geochemistry and mineralogy

The range in the whole-rock F contents for all Orijärvi samples is 150–3550 ppm (Fig. 3, Table 1). Cordierite–anthophyllite rocks contain 950–2450 ppm F and have slightly enriched rare earth elements (REE) with negative Eu anomalies. The F content in minerals from sample LMR 34c was 2.71–2.74 wt% in apatite, 0.57–0.83 wt% in phlogopite, 0.08–0.20 wt% in anthophyllite and <0.13 wt% in chlorite.

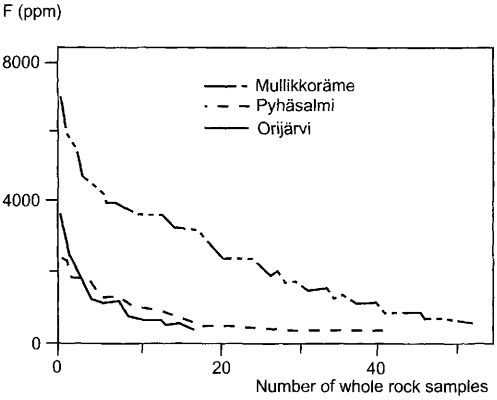

Fig. 3. F contents in rock samples (not as geographical trend) from the Orijärvi, Pyhäsalmi and Mullikkoräme Zn–Cu–Pb deposits

Cordierite–biotite and garnet–biotite gneisses contain 400–3550 ppm F. Cordierite–biotite gneisses show more enriched and fractioned light REE (LREE) than garnet–biotite gneisses. The F content in samples from a concordant amphibolite unit (previously described as subvolcanic mafic sill: Mäkelä 1983) was 200–450 ppm. These samples have low Cu, Zn and Pb contents, with the exception of one sample from the Orijärvi mine area. In the amphibolite samples ($n = 3$), which are also characterized by low metal contents, F correlates positively with FeO ($r^2 = 1.00$) and K_2O ($r^2 = 0.95$), but negatively with Na_2O ($r^2 = 0.98$) and SiO_2 ($r^2 = 0.91$). The amphibolite data also show a positive correlation between F and total metal content (Cu + Zn + Pb; $r^2 = 0.96$). Hence, hydrothermal activity of an F-rich fluid may have caused the variation in major elements as well as the local enrichment in Cu, Zn and Pb. These preliminary results are augmented by the extensive geochemical databases of the Outokumpu Mining Ltd (see next section).

Mineral assemblages in probed samples from Orijärvi are: anthophyllite + chlorite + Zn-rich spinel; anthophyllite + biotite + cordierite + quartz ± Zn-rich spinel; biotite + hornblende + muscovite + quartz + plagioclase; and biotite + anthophyllite quartz + plagioclase ± chlorite.

Sample ORI62b contains the last assemblage with additional gedrite and minor supersolvus orthoamphibole intermediate between anthophyllite and gedrite (Table 2). The order of decreasing X_F (normalized to biotite) in biotite-bearing samples is (see also Tables 2 and 3): biotite (X_F range: 0.011–0.106, $n = 49$) > gedrite (0.006–0.026, $n = 11$) > intermediate supersolvus orthoamphibole (0.009–0.020, $n = 12$) > anthophyllite (0.006–0.026, $n = 26$) > hornblende (0.003–0.010, $n = 6$) ~ muscovite (0.006, $n = 1$) > chlorite (0.001–0.012, $n = 11$). Surprisingly, the highest recorded F content is for anthophyllite (X_F range: 0.047–0.132) in sample LMR35e, which lacks biotite.

Mineral assemblages in probed samples from Iilijärvi are (see also Tables 2 and 3): anthophyllite + biotite ± intermediate supersolvus orthoamphibole ± cummingtonite (± quartz ± plagioclase). The order of decreasing X_F (normalized to biotite) is: biotite (X_F range: 0.006–0.074, $n = 31$) > intermediate supersolvus orthoamphibole (0.002–0.027, $n = 8$) ~ anthophyllite (0.002–0.029, $n = 16$).

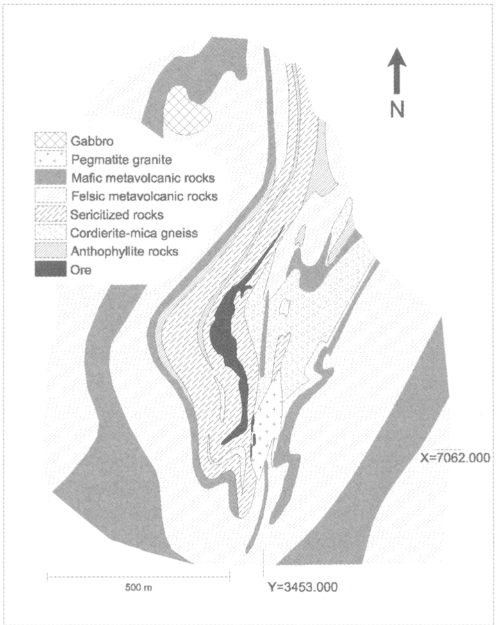

Fig. 4. Geological sketch map of the Pyhäsalmi area (after Ekberg & Penttilä 1986)

Pyhäsalmi & Mullikkoräme deposits, central Finland

Regional background

The Pyhäsalmi and Mullikkoräme mines are situated in central Finland, *c.* 160 km SSE of Oulu (Figs 1 and 4), within the Raahe–Ladoga Zone. The Raahe–Ladoga Zone, previously called the Main Sulphide Ore Belt, has been described as a collisional boundary zone between Archaean and Proterozoic crustal domains (Lahtinen 1994). It is the main metallogenic zone in Finland where five principal phases of mineralization have been recorded (Ekdahl 1993; Weihed & Mäki 1997). The Pyhäsalmi and Mullikkoräme mines occur within the Pyhäsalmi volcanic complex, a local unit of the larger Pyhäsalmi Island Arc, which forms a 10–30 km wide and *c.* 350 km long zone including over 60 significant mineral deposits. According to Ekdahl (1993), ore deposits in the Pyhäsalmi Island Arc are characterized by (i) medium- to high-grade metavolcanic zones and complexes, (ii) submarine, tholeiitic and calc-alkaline island arc volcanism, (iii) vertical or lateral hydrothermal alteration characterized by sericitization, silicification, chloritization, the presence of garnet–cordierite–anthophyllite rocks and (iv) the Mg, Fe, H_2O and S enrichment and Si, Ca, Na and K depletion towards the ore bodies.

The Pyhäsalmi type ore deposits are thought to have formed during the early orogenic stage of the Svecofennian orogen at *c.* 1.92 Ga (Ekdahl 1996). Volcanism is bimodal in style: most of the felsic rocks are calc-alkaline, low-K rhyolites, whereas mafic volcanic rocks are sub-alkalic, resembling present day low-K tholeiitic basalts to basaltic andesites (Kousa & Lundqvist 2000). The lower stratigraphic levels are dominated by felsic mass flows or tuffaceous and pyroclastic rocks with mafic intercalations. Mafic lavas and pyroclastic rocks, pillow lavas and breccias become more abundant at higher stratigraphic levels (Kousa & Lundqvist 2000). Lahtinen (1994) suggested that the felsic rocks and associated VMS deposits represent an aborted rifting stage in an island arc environment. According to Weihed & Mäki (1997), volcanism started in an extensional continental margin with felsic volcanism and continued in a rifted marine environment with mafic volcanism. According to these authors, large-scale hydrothermal alteration and ore formation occurred near the centres of mafic volcanism. The metavolcanic rocks have later been intruded by syn-tectonic intrusions (Kousa *et al.* 1994; Lahtinen & Huhma 1997; Kousa & Lundqvist 2000).

In the Pyhäsalmi mine area, the volcanogenic host rocks of the ore bodies have undergone amphibolite facies metamorphism and pervasive deformation resulting in sericite schists and quartzites, cordierite and sillimanite gneisses and cordierite-, anthophyllite- and garnet-bearing rocks (Huhtala 1979). Peak metamorphic conditions reached 600–700 °C and 5–7 kbar (A.-P. Tapio, pers. comm. 2000). The Pyhäsalmi ore deposit is a typical VMS deposit surrounded by a hydrothermal alteration halo. All rock types are most intensely altered near the ore bodies, but the width of the alteration zone differs from 300 m at the surface to a few metres at deeper levels (Weihed & Mäki 1997). The ore contains *c.* 70% sulphides, mainly pyrite, chalcopyrite, sphalerite and pyrrhotite; common accessory minerals are galena, magnetite and arsenopyrite (Helovuori 1979; Weihed & Mäki 1997). Production from the start-up date (1962) to the present day has been about 33.4 Mt with levels of 2.48% Zn, 0.8% Cu and 35.2% S. A new ore body at greater depth was discovered at the end of 1996 with reserves indicating 17 Mt with levels of 2.1% Zn, 1.1% Cu and 34.2% S (Weihed & Mäki 1997; Mäki & Puustjärvi 2002).

The Mullikkoräme mine is located in one of three satellite deposits, 7 km east of the main Pyhäsalmi mine. Host rocks in mineralized zones are mainly chloritized and sericitized cordierite–amphibole gneisses and other altered felsic to mafic volcanites. Locally, felsic volcanic rocks with talc–chlorite schist intercalations are abundant. The metamorphic grade reaches greenschist facies, which is considerably lower than in Pyhäsalmi (Weihed & Mäki 1997). Based on the reported mineral assemblage, andalusite + biotite + chlorite, our temperature estimate is 500–560 °C at a pressure of 1–3 kbar, using published KFMASH grids (e.g. Spear & Cheney 1989). The mine was closed in 2000 after a total production of 1.2 Mt in its ten-year history, at an average grade of 0.23% Cu, 5.99% Zn, 0.62% Pb, 1.21 $g\,t^{-1}$ Au, and 33 $g\,t^{-1}$ Ag (Mäki & Puustjärvi 2002). Mineralized horizons at Mullikkoräme consist of massive sulphides, with pyrite, sphalerite, galena and chalcopyrite as common ore minerals; gangue minerals are quartz, talc, carbonate, Fe–Mg silicates and barite (Weihed & Mäki 1997).

Petrography

The most common silicate minerals in Mullikkoräme samples are biotite, chlorite and muscovite, garnet, andalusite and plagioclase. Cordierite and hornblende are present in some sections. Observed mineral assemblages are biotite + chlorite + garnet + plagioclase + quartz ± anthophyllite; biotite + chlorite + hornblende + plagioclase + quartz; biotite + andalusite + cordierite + quartz + tourmaline; and biotite + chlorite + andalusite + garnet + muscovite + staurolite + plagioclase + quartz. 'Skarn' samples (possibly metamarls or altered ultramafics) contain talc, muscovite, spinel, chlorite, tremolite and carbonate minerals. Beside sulphide minerals, our Pyhäsalmi samples contain the assemblages tourmaline + muscovite ± biotite; biotite + chlorite + hornblende + talc; biotite + hornblende ± apatite. A.-P. Tapio (pers. comm. 2000) also reported anthophyllite + Zn-rich staurolite ± sillimanite + quartz ± biotite ± cordierite.

Geochemistry and mineralogy

A significant number ($n = 52$) of F analyses exist of whole-rock samples from the Mullikkoräme mine. The F contents in those rocks are 300–7100 ppm (Table 1, Fig. 3), significantly higher than in Orijärvi. This difference is also reflected in the mineralogy: the average F content of biotites from Mullikkoräme is 0.22 wt%, whereas it is only 0.12 wt% in biotites from Orijärvi. Samples from the nearby Pyhäsalmi mine have lower whole-rock F contents, namely 55–2300 ppm (Fig. 3), which is a similar range as in Orijärvi. This may be due to mineralogical constraints (see below), as the Pyhäsalmi samples have higher ore contents.

The hydrous minerals in the Pyhäsalmi samples are biotite, chlorite, muscovite, hornblende, talc, tourmaline and apatite. The highest recorded F content is in apatite from Pyhäsalmi sample 208, ($X_F = 0.328$–0.340, $n = 2$), much higher than coexisting biotite ($X_F = 0.030 \pm 0.004$, $n = 4$). Tourmaline ($X_F = 0.078 \pm 0.041$, $n = 4$) has slightly higher F content than coexisting biotite ($X_F = 0.074 \pm 0.006$, $n = 10$) in sample 168. Talc ($X_F = 0.015 \pm 0.004$, $n = 10$) has slightly lower F content than coexisting biotite ($X_F = 0.018 \pm 0.010$, $n = 3$) in sample 181. X_F of Hbl is 10–30% lower than that of coexisting biotite. F contents are still lower in muscovite and negligible in chlorite.

The hydrous minerals at Mullikkoräme are biotite, chlorite, muscovite, hornblende, talc, anthophyllite, tourmaline and staurolite. F contents are low in chlorite ($X_F = 0.002 \pm 0.001$, $n = 7$), but significantly higher in biotite ($X_F = 0.015 \pm 0.006$, $n = 25$), muscovite ($X_F = 0.008 \pm 0.003$, $n = 11$) and hornblende ($X_F = 0.007 \pm 0.004$, $n = 5$). Hence, the last two seem to be the main F carrier minerals in view of the low fluorite abundance. Tourmaline ($X_F = 0.028$–0.033, $n = 2$) and staurolite ($X_F = 0.009$, $n = 1$) have fairly high fluorine contents, but they are relatively rare. No talc and anthophyllite analyses exist for this area. The highest F contents occur in talc-rich rocks with $X_{Mg} > 0.8$, which probably represent highly altered mafic rocks, so talc may also be a significant F carrier mineral (see Pyhäsalmi data). F contents in anthophyllite are expected to be as low as elsewhere.

The main S-bearing minerals in the Mullikkoräme mine are pyrite, sphalerite, galena, chalcopyrite and barite. Using these mineralogical constraints, the amount of Fe residing in sulphides can be estimated and the total weight corrected for the lower amount of iron oxide (Table 1). The results show that on average 60 ± 16% of the Fe resides in sulphides, giving a strong positive correlation between Fe and S contents of the samples (Fig. 5). Geochemical data from a 30 m long drill core through a metal rich horizon in the Mullikkoräme Zn–Cu–Pb deposit show a positive correlation between F and X_{Mg} [= MgO/(MgO + FeO)], without correcting for ferric iron (Fig. 6). This suggests that leaching of corrosive, F-bearing fluids has reduced the iron content of this rock suite. The data also show a moderately strong, negative correlation between F and total metal content (Pb + Zn + Cu + Fe; Fig. 6). Hence, this metal rich zone (metal sink) seems to show a trend that is opposite to the trend of metal poor zones (metal sources ?) in Orijärvi (see also below).

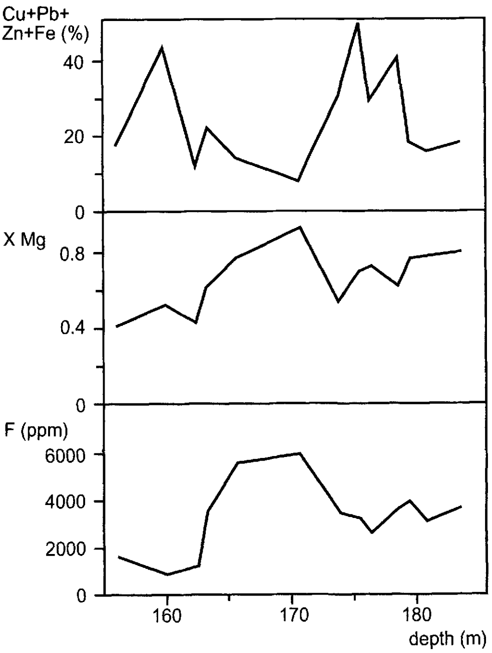

Fig. 6. Positive correlation between F (ppm) and X_{Mg} [= MgO/(MgO + FeO)] and moderately strong, negative correlation between F (ppm) and total metal content (wt%) in a drill core through the Mullikkoräme Zn–Cu–Pb deposit

Considering all samples from Mullikkoräme for which F was measured ($n = 52$), the positive correlation ($r = 0.85$) between F and X_{Mg} (Fig. 7a) is confirmed. A plot of F against metal content (Fig. 7b) shows a similar, negative correlation as the drill core data (Fig. 6), but with considerable scatter. F also shows a negative correlation with S content (Fig. 7c). At first sight the data would therefore suggest that the higher the F flux through the system, the lower the content of sulphide ore, at odds with the commonly observed increase of F content towards ore bodies (e.g., Lavery 1985). However, this is only *apparent* because of the interplay of two factors: (i) the closure problem in geochemical data (e.g. Rollinson 1993) and (ii) the mineralogical constraint that F is dominantly incorporated into hydrous silicates. The more sulphide a sample contains, the less silicates are present and the less F can be accommodated in the rock, even when F concentrations in F carrier minerals may be high. This may also explain why the ore-rich Pyhäsalmi samples have lower F contents (Fig. 3).

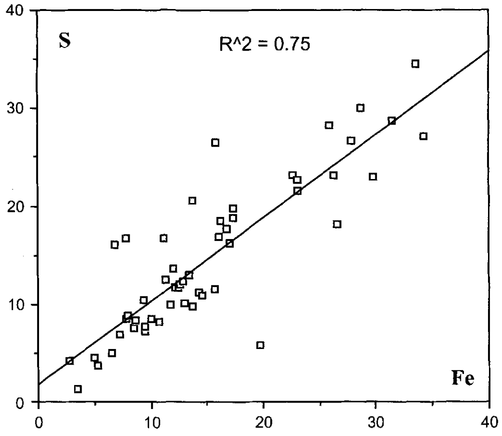

Fig. 5. Positive correlation between Fe and S (element wt%) in the Mullikkoräme samples, confirming that Fe occurs dominantly in the form of sulphides (mainly pyrite and chalcopyrite)

To circumvent the closure problem, it is useful to normalize element concentrations to elements of relatively low mobility such as Ti, Al (and Mg, to a lesser extent). Ti and Al show a strong positive correlation (Fig. 8a), suggesting similar geochemical behaviour. Combining TiO_2, Al_2O_3 and MgO as the total mass of relatively immobile elements not or very little affected by whole-rock alteration, some clear correlations become apparent. F correlates positively with the sum of these relatively immobile elements (Fig. 8b), whereas Fe shows a negative correlation (Fig. 8c). Hence, leaching by F-rich fluids probably led to lower Fe concentrations and an increase in the concentration of immobile elements Ti, Al and Mg. This

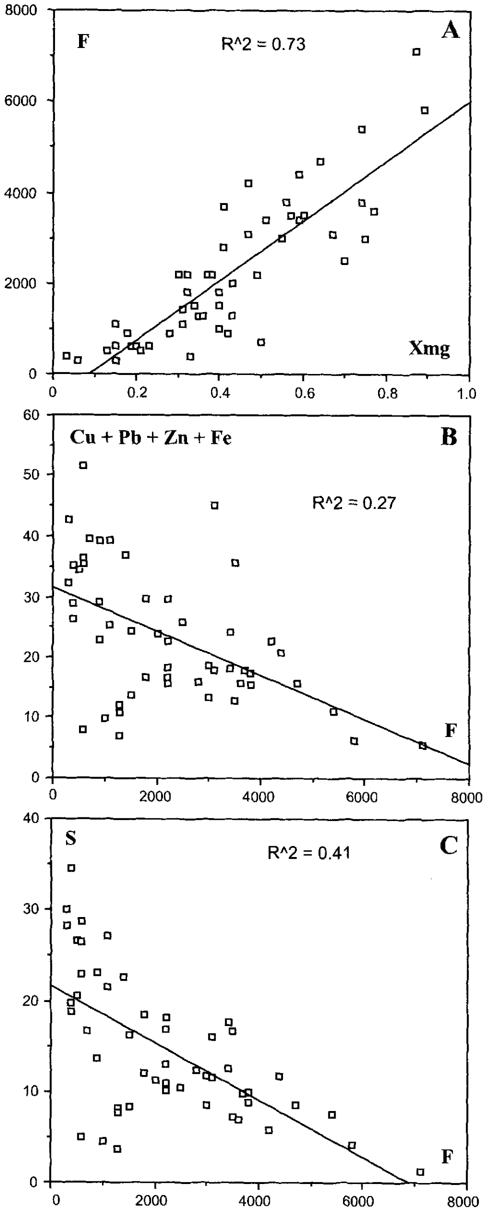

Fig. 7. Mullikkoräme samples show a strong positive correlation between F (ppm) and X_{Mg} [= MgO/(MgO + FeO)], where all iron is taken as FeO (**a**), and a negative correlation between F (ppm) and the total metal content (wt%), with considerable scatter (**b**). F (ppm) and S (wt%) show a negative correlation (**c**)

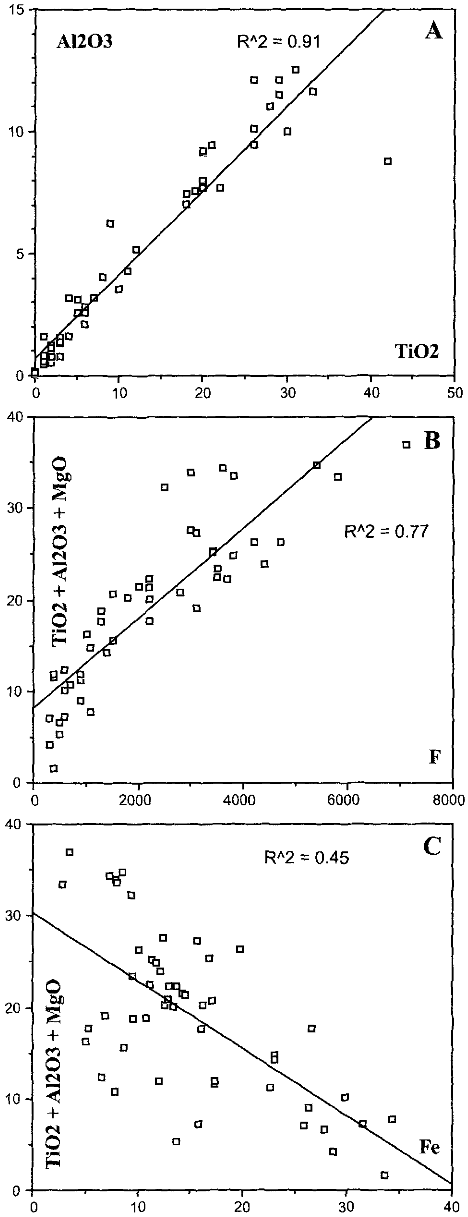

Fig. 8. Immobile oxides TiO_2 and Al_2O_3 (wt%) correlate positively (**a**), suggesting similar geochemical behaviour. F (ppm) shows a positive (**b**) and Fe (wt%) a negative (**c**) correlation with the sum of immobile elements (wt%)

strengthens the interpretation of the F versus X_{Mg} diagrams (Figs 6 and 7a). Normalizing to the immobile elements, F correlates positively with the total metal content (Fig. 9). This correlation is quite strong when normalized to TiO_2 (Fig. 9a) and moderate when normalized to Al_2O_3 (Fig. 9b). Viewed in this way, the data seem to suggest that a higher F flux through the system corresponds to a higher content of sulphide ore, consistent with the increase of F content towards ore bodies (e.g., Lavery 1985).

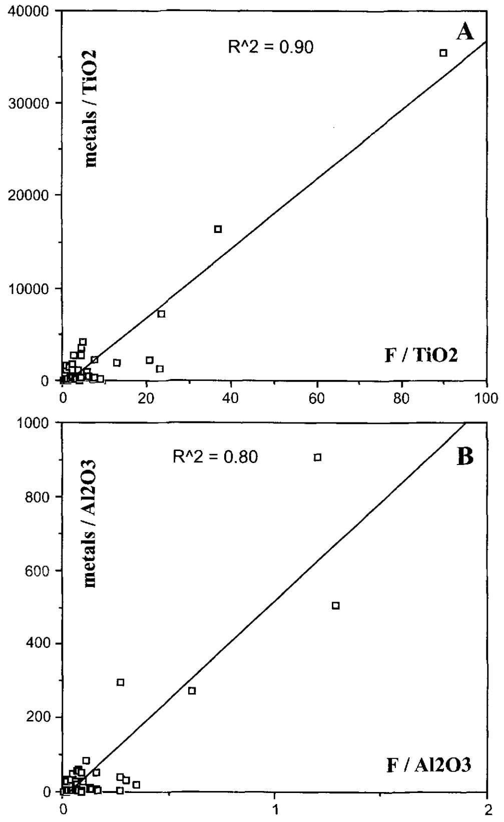

Fig. 9. Normalized to immobile elements (TiO_2 in **a**; Al_2O_3 in **b**), total metal content and F correlate positively (all data in wt%)

Oonagalabi domain, Arunta block, central Australia

Regional background

The Oonagalabi domain is located in the western Harts Range, about 50 km east of the Strangways Complex in the eastern Arunta Block, Central Australia. It comprises a succession of orthogneisses and subordinate supracrustal units (Sivell 1986) that were metamorphosed under transitional amphibolite to granulite facies conditions (Oliver *et al.* 1988; Raith & Kriegsman 1998). The Oonagalabi domain displays a fold nappe geometry (Ding & James 1985) and has been interpreted as a tectonic window to granulites underlying the amphibolite facies rocks of the Eastern Harts Range. All units record the same deformation stages, being top-to-the-SW thrusting and subsequent refolding into NE-plunging folds with NE-trending, subvertical axial planes. The Oonagalabi domain hosts a small, sub-economic Pb–Zn–Cu deposit where most of our samples have been collected. Peak metamorphism, which also affected these orthoamphibole dominated units, culminated at *c.* 750–800 °C, 8–9 kbar (Raith & Kriegsman 1998).

Petrography

Aluminous lenses in a concordant orthoamphibole dominated unit show an early assemblage gedrite + spinel ± corundum, overgrown by sapphirine and garnet. The earliest recorded mineral assemblage in K-poor felsic rocks is gedrite + sillimanite + quartz, overprinted by garnet and cordierite. Locally, gedrite has broken down to orthopyroxene + garnet + quartz and the orthopyroxene is overgrown at the edges by small (retrograde) anthophyllite grains. Rocks closest to the Pb–Zn–Cu deposit are dominated by retrograde anthophyllite with orthopyroxene relics. Details are given in Raith & Kriegsman (1998) and a paper in preparation.

Geochemistry and mineralogy

The high F content of gedrite (0.3–0.8 wt%), phlogopite (0.9–2.1 wt%) and anthophyllite (up to 0.3 wt%), and the presence of fluorite in marble layers and chondrodite (with 3.3–3.8 wt% F) in some orthoamphibole dominated lenses, suggest a high F content of the hydrous fluids that have affected the deposit. Zn content is highest (up to 12.5 wt% ZnO) in spinel from chondrodite bearing lenses, strengthening the link between Zn mineralization and F. A reference sample several kilometres away from the deposit, with the assemblage orthopyroxene + garnet + quartz + biotite + plagioclase + rutile (+ retrograde anthophyllite), contains biotite with only *c.* 0.14 wt% F, much lower than near the ore deposit.

There are few whole-rock chemical analyses from this area, but available microprobe data and modal abundances can be used to estimate the F content of some samples. Sample AR125 contains *c.* 60 vol% gedrite (at 0.74 wt% F) and 10 vol% chondrodite (at 3.6 wt% F), yielding an estimated 8000 ppm F in the rock. Sample AR126c contains *c.*40 vol% phlogopite (at 2 wt% F) and consequently has a similar F content. Sample AR126d contains about 80 vol% anthophyllite (at 0.15 wt% F), giving an estimated 1200 ppm F. Sample AR129 contains *c.*2 vol% gedrite (at 0.7 wt% F) and 0.5 vol% biotite (at 1 wt% F), equating with an estimated 1450 ppm F. Sample AR245 contains *c.* 15 vol% gedrite (at 0.64 wt% F), corresponding to an estimated 960 ppm F in the rock; this is consistent with a whole-rock analysis of 950 ppm. The range of whole-rock F contents in Oonagalabi is therefore *c.* 1000–8000 ppm, quite similar to the range of values at Mullikkoräme mine.

F partitioning data and F carrier minerals

Figure 10 shows X_F = [F/(F + OH)] data for coexisting biotite and orthoamphiboles. The data for anthophyllite in samples from Finland (Orijärvi and Iilijärvi) and Oonagalabi fall on different lines, with the slope of the Oonagalabi line closer to $K_D = 1$ (Fig. 10a). Within both areas, X_{Mg} increases with overall F content, without affecting the K_D of F partitioning. In view of the well-documented influence of X_{Mg} on the F content of hydrous minerals (e.g., Rosenberg & Foit 1977), the constant K_D for F partitioning implies that anthophyllite shows a similar Fe^{2+}/Fe avoidance as biotite. The data suggest that peak temperature (500–650 °C in Finnish samples: Schreurs & Westra 1985; Schneiderman & Tracy 1991; 750–800 °C in Oonagalabi: Raith & Kriegsman 1998) is the dominant factor controlling F partitioning. X_F data for biotite coexisting with gedrite (Orijärvi and Oonagalabi) show a similar pattern (Fig. 10b). In the Oonagalabi samples, X_{Mg} increases with overall F content, without affecting the K_D of F partitioning. The Oonagalabi line has a higher slope than the Finnish line, consistent with higher peak temperatures in the former.

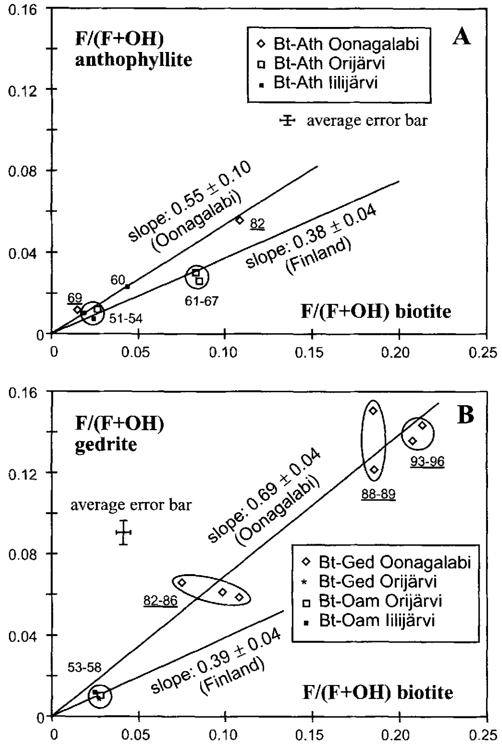

Fig. 10. F partitioning between orthoamphiboles (Ath, anthophyllite; Ged, gedrite; Oam, intermediate, supersolvus orthoamphibole) and biotite (Bt). Numbers near (groups of) average analyses indicate Mg numbers = 100 × X_{Mg} (underlined: Oonagalabi data)

The slope for biotite–gedrite is significantly higher than for biotite–anthophyllite in Oonagalabi; Fig. 10a, b). Hence, combining these data, the order of decreasing X_F for coexisting biotite and orthoamphiboles is: biotite > gedrite > anthophyllite. Intermediate, supersolvus orthoamphiboles (Finnish samples) plot close to the single Finnish gedrite point. As for other minerals, chlorites in Finnish samples have F contents close to 0 even in samples where biotite has significant F contents, showing that it is not an important F carrier mineral. An interesting observation, however, is that chlorite inclusions in garnet in Orijärvi sample 62b show higher F contents (0.034 wt%) than texturally late, retrograde, chlorite (0.006 wt%; Table 3), which suggests that the prevailing fluid was more F-rich prior to peak metamorphism than on the retrograde path. Hornblende and muscovite in Mullikkoräme and Pyhäsalmi samples have much lower X_F than coexisting biotite, but higher F contents than chlorite. Talc analysed so far had F contents comparable to hornblende (X_F = 0.015 and 0.016, respectively, in Pyhäsalmi) but a sample from Mullikkoräme with very high bulk F content (7100 ppm) is dominated by talc and we suspect it may be the main F carrier mineral there.

Apatite (Pyhäsalmi sample 208) and chondrodite (Oonagalabi sample AR125) have much higher F contents than coexisting phlogopite, with X_F up to 0.3. The relative F order of preference between apatite and chondrodite can be estimated indirectly. In sample AR125, X_F in chondrodite (0.322 ± 0.013) is twice as high as in gedrite (0.160 ± 0.012). This is the only Oonagalabi sample without biotite, but using the average K_D for F exchange between biotite and gedrite (from Fig. 10b), the X_F value for coexisting biotite is estimated at 0.24 ± 0.04. In Pyhäsalmi sample 208, X_F in apatite is 0.334 ± 0.009, whereas the biotite X_F is only 0.030 ± 0.004. This suggests that, when normalized to biotite X_F, apatite has a much higher preference for F than chondrodite.

Combining all data, the relative F partitioning order of hydrous minerals is apatite > chondrodite > biotite > gedrite > (hornblende, muscovite, anthophyllite) > chlorite. The F partitioning between hornblende, muscovite and anthophyllite is still unclear. Our data on talc, staurolite and tourmaline are also inconclusive because of the low number of analyses. The F partitioning data can be used to quickly identify the F carrier mineral in any rock type, by estimating the modal abundance of each mineral in thin section or hand specimen. The Orijärvi samples contain principally anthophyllite, whereas gedrite is very common in Oonagalabi. This probably reflects a combination of different bulk compositions and different peak metamorphic temperatures. As our data show that anthophyllite has a much lower F content (up to 0.3 wt%) than gedrite (up to 0.8 wt%), much less F can be accommodated in orthoamphiboles at Orijärvi than at Oonagalabi.

For some samples or suites of samples, both mineral and whole-rock chemical analyses were obtained, allowing a more precise determination of the main F carrier minerals. For example, sample LMR 34c (cordierite–anthophyllite rock) from Orijärvi contains 2450 ppm (=0.245 wt%) F based on whole-rock analysis. Sample LMR 34b (cordierite–anthophyllite gneiss), which was sampled 10 m away in the same rock unit, contains biotite (0.77 wt% F: Table 2), anthophyllite (0.16 wt%: Table 2) and chlorite (0.13 wt%). The approximate F content for this sample (at 30% biotite, 30% anthophyllite, 30% cordierite, 1% chlorite and 9% anhydrous minerals) is 0.28 wt%, similar to the analytical value of the adjacent sample. Biotite contributes 0.23 wt% and is thus the main F carrier mineral in cordierite–anthophyllite rocks and gneisses. Other rock types usually have much less biotite, but plenty of fluorite, which suggests that fluorite is the most important F-bearing mineral in those medium-grade rock types. In contrast, orthoamphiboles are the dominant F-bearing minerals in the transitional granulite facies rocks at Oonagalabi, where fluorite is absent (except in marbles). Anthophyllite is the dominant mineral in the deposit and thus the main F carrier on the regional scale. However, chondrodite, gedrite and phlogopite are the main F carriers in other samples.

Discussion

F content and metamorphic grade

A comparison of whole-rock samples from Orijärvi, Pyhäsalmi and Mullikkoräme shows that the Mullikkoräme samples have exceptionally high F contents (Fig. 3). As Mullikkoräme is the only low-grade metamorphic area of the three, one could conclude that significant amounts of F have left the system during peak metamorphism in Orijärvi and Pyhäsalmi. However, the Oonagalabi samples (see above) show similar F contents as in Mullikkoräme, even though the peak metamorphic temperatures were *c.* 750–800 °C. As mineral–fluid partitioning coefficients for F indicate that F will remain in solids at least until advanced partial melting (Anfilogov *et al.* 1977; Zhu & Sverjensky 1991), the whole-rock data probably reflect F contents prior to the peak metamorphic overprint.

Timing of F influx

High F contents of magmatic rocks are a feature typical of so-called anorogenic granitoids (e.g. Rogers & Satterfield 1994; Goodenough *et al.* 2000). In the Svecofennian orogen of Finland, this may be either early orogenic (e.g., Orijärvi back-arc basin: Väisänen 2001), late-orogenic (post-collisional: Eklund *et al.* 1998), or post-orogenic (e.g., rapakivi granites: papers in Haapala & Rämö 1999). As a result, ore deposits related to high F flux are probably either early orogenic or late- to post-orogenic. These relative timings are easy to distinguish, because early orogenic intrusions predate peak metamorphism, whereas late- to post-orogenic intrusions post-date peak metamorphism. Arguments for early F influx in the deposits studied here, are:

1 fluorite, apatite and oriented F-rich biotite form inclusions in peak metamorphic porphyroblasts (garnet, cordierite);
2 chlorite inclusions in garnet show higher F contents than texturally late, retrograde chlorite;
3 volcanics and related granitoids that are possible F sources, predate peak metamorphism (Orijärvi: Väisänen 2001; Oonagalabi: Sivell 1986); at Orijärvi, extrusion of rhyolite and coeval intrusion predate peak metamorphism by some 50–60 Ma.

Correlation of F with ore minerals

Our data superficially suggest that a higher F flux through a system results in lower contents of sulphide ore, which is inconsistent with the commonly observed increase of F content towards ore bodies (e.g. Lavery 1985). However, we have shown that this is due to a mineralogical constraint, F being dominantly incorporated into hydrous silicates, in combination with the closure problem in geochemical data. When normalized to relatively immobile elements (Ti, Al), F correlates positively with the total metal content, as expected.

A similar feature can be seen in the Crandon Cu–Zn deposit (Lavery 1985, fig. 4): the F content increases towards the deposit, but drops sharply at the point where Cu and Zn sulphides start to dominate the mineralogy; small Cu and Zn peaks within the deposit also correlate with low values of F. We believe that this is due to the same geochemical and mineralogical complications observed in our data and that it could be solved in a similar manner. Hence, geographical F trends may become clearer when normalized to immobile elements, which may improve geochemical exploration for Pb–Zn–Cu deposits.

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