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Pentti Rehtijärvi

Distributions of phosphorus, sulphur and sulphur isotopes in a strata-bound base metal deposit, Kangasjärvi, Finland

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The Kangasjärvi strata-bound massive base metal deposit is located in the Vihanti-Pyhäsalmi-Pielavesi Zn-Cu ore province, Finland, and is hosted by a succession of metamorphosed, calc-alkaline and tholeitic volcanogenic rocks and their altered derivatives. Alteration is attributed to hydrothermal processes considered to be related to ore deposition. Metamorphic mineral assemblages, particularly garnet-cordierite-sillimanite and garnet-cordierite-anthophyllite, reflect the altered chemical composition. The relatively unaltered mafic, intermediate and felsic volcanogenic gneisses average 0.14 %, 0.25 % and 0.07 % P_2O_5, respectively. The P_2O_5 means in their altered derivatives are systematically lower, 0.10 %, 0.10 % and 0.05 %. Phosphorus is mainly contained in euhedral metamorphic apatite.

The P_2O_5 content shows a marked negative halo-type distribution around the massive sulphides. The pattern is approximately inverse to the patterns of sulphur content and the calculated alteration index of $(MgO + K_2O) / (MgO + K_2O + CaO + Na_2O)$. The correlation of P_2O_5 to ln(S) changes in d.d. cores from —0.70 near the earth surface to —0.20 below the massive sulphides. This together with the distribution patterns is considered to indicate leaching of phosphorus in processes related to ore deposition and the direction of introduction of acid altering fluids.

The average pyrite $\delta^{34}S$ value in the massive sulphides is 7.0 ‰. The $\delta^{34}S$ pattern shows isotopic lightening to a minimum of —13.7 ‰ after the massive sulphide deposition. The lightening is considered to reflect a pre-metamorphic change in the isotope composition and to be related to a stratigraphic height where sulphur precipitation as sulphate was increased. The pattern is consistent with that found to characterize isotopic sulphur distribution in Kuroko-type deposits.

The results are compared with results from Vihanti, where in a more distal environment high contents of phosphours, uranium and iron characterize the bottom units in a sequence of volcanogenic gneisses, dolomites and skarns hosting a base metal ore complex.

Key words: geochemistry, strata-bound deposits, base metals, phosphours, sulfur, isotopes, S-34/S-32, host rocks, metavolcanic rocks, Proterozoic, Keitele, Kangasjärvi, Finland.

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INTRODUCTION

Geological setting

The Kangasjärvi strata-bound massive sphalerite-pyrite deposit is located in the Vihanti-Pyhäsalmi-Pielavesi Zn-Cu ore province (Huhtala 1979). The province lies in the boundary zone between the Archean basement complex and Proterozoic Svecokarelian rocks (Fig. 1) and forms the northwestern part of the Main Sulphide Ore Belt (Kahma 1973, Kahma *et al.* 1976) which runs from Lake Ladoga to the northern end of the Gulf of Bothnia.

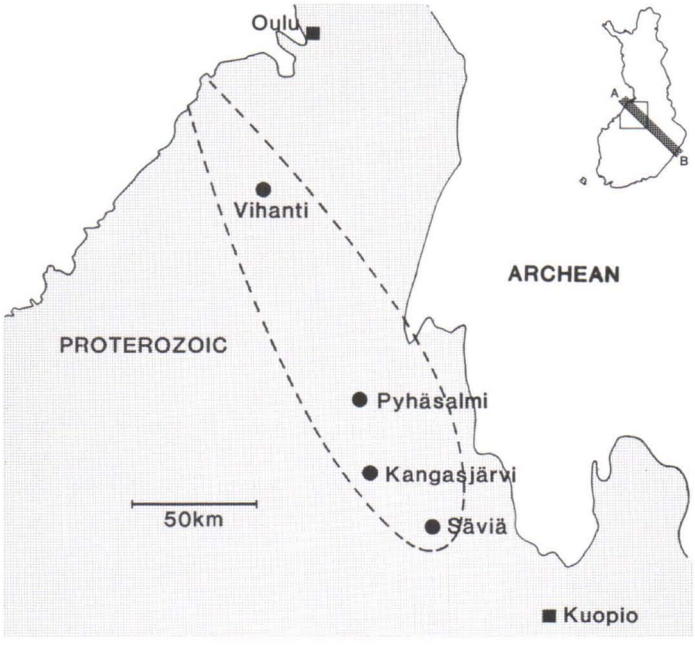

Fig. 1. Location of the Kangasjärvi deposit in the Vihanti-Pyhäsalmi-Pielavesi Zn-Cu ore province, western Finland. A-B shows the Main Sulphide Ore Belt (Kahma *et al.* 1976).

Radiometric ages of 1850—1900 Ma, corresponding to the main phases of Svecokarelian folding and metamorphism, have been determined for volcanic rocks (Simonen 1980). Vaasjoki (1981) considers 1880 Ma to 1940 Ma the most likely time interval for deposition of ores in the Main Sulphide Ore Belt. According to the plumbotectonic model presented by Doe and Zartman (1979), the lead in the polymetallic ores at Vihanti, Pyhäsalmi and Säviä is of mantle origin, but there is also some influence of adjacent sediments and cratonic rocks (Stacey *et al.* 1977, Vaasjoki 1981). This argument can well be extended to the Kangasjärvi deposit, which is both very similar to the Pyhäsalmi ore deposit and may even lie in the same volcanogenic belt. All four deposits can be considered as strata-bound, massive and volcanic- exhalative in origin (cf. Helovuori 1979, Huhtala 1979, Rauhamäki *et al.* 1980).

Lithology

The Kangasjärvi deposit is hosted by a succession of mafic, intermediate and felsic volcanogenic rocks and their altered derivatives. A preliminary lithological map of the Kangasjärvi area is given in Fig. 2. The regional geology has been described by Salli (1983) and Huhtala (1979), among others. The homogenous appearance and texture of the intermediate rocks SE of the ore deposit suggest them to be former lavas. Altered rocks and relatively thin interlayers of small- and even-grained quartz-feldspar gneisses are considered on the basis of their bedded appearance to be metamorphic derivatives of basic, intermediate and acid tuffs. Pre-metamorphic changes in chemical compositions are

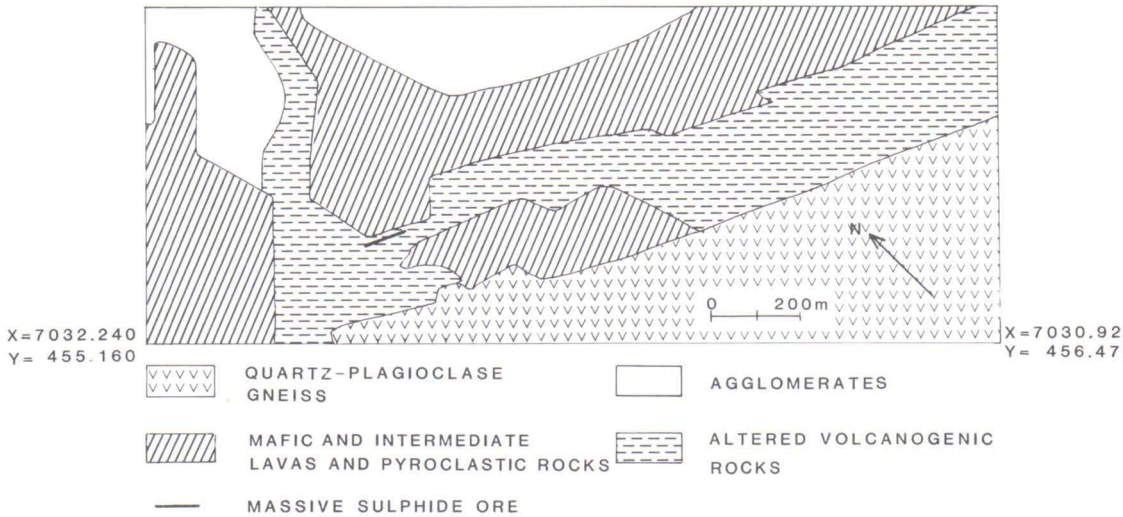

Fig. 2. Lithologic map of the Kangasjärvi area. Compiled by J. Nikander.

reflected in metamorphic mineral assemblages, such as garnet-cordierite-sillimanite and garnet-cordierite-anthophyllite. The alteration in the Pyhäsalmi-Säviä area is attributed to the same hydrothermal processes that formed the massive sulphides (Huhtala 1979). At least near the ore deposit the volcanogenic succession is characterized for instance by magnesium enrichment and by lack of carbonate minerals, indicating a proximal environment of deposition (cf. Plimer 1978). The succession is overlain by quartz-plagioclase gneiss (Figs. 2, 4, 5 and 6) which is a medium- to coarse-grained gneissic rock with granitoid characteristics. A calc-alkaline trend for the volcanogenic rocks hosting the Pyhäsalmi ore deposit has been proposed by Helovuori (1979). Calc-alkaline rocks are also dominant at Kangasjärvi. A tholeitic suite is, however, suggested for the relatively unaltered mafic rocks on the basis of bulk chemical analysis.

Sulphide layers are characterized by a transverse metal zonation Cu-Zn: both the content of Zn and the Zn/Cu ratio are increased in the footwall of the orebodies. The rock sequence is thus considered to have been overturned during postdepositional folding. In addition to pyrite and sphalerite, chalcopyrite and pyrrhotite are present as disseminations and veins. Galena is rare. The massive sulphide layers contain about 400 000 t of ore, averaging 3.2 % Zn and 0.13 % Cu.

SAMPLING AND ANALYTICAL METHODS

Sampling was done by the chip-channel method from a vertical diamond drill core profile (Fig. 3). Four to six samples of 10 cm length were taken from the diamond drill cores to represent 5 m or less of the core and ground together to give a sample of a particular rock type. The samples were analyzed for P_2O_5, FeO and S by XRF, using pressed discs, in the Geological Laboratory of Outokumpu Oy in Espoo. In addition, 55 concentrates of pyrite were extracted from core 27 for sulphur isotope study. Each of the extractions represented 2 to 10 cm of the diamond drill core. The isotope determinations were made with a Varian GD 150 mass spectrometer at the Laboratory of Economic Geology, Helsinki University of Technology, Espoo, using methods described and developed by Mäkelä and Tammenmaa (1977). The accuracy of the determinations is estimated to be ± 0.1 ‰. The extractions included disseminations, veins and massive types of pyrite.

Weighted moving averages of three values within a lithological unit have been used in figured plots (excluding the $\delta^{34}S$ data). The major element contents have been normalized by linear transformation between 1 and 10 before computing the ratios.

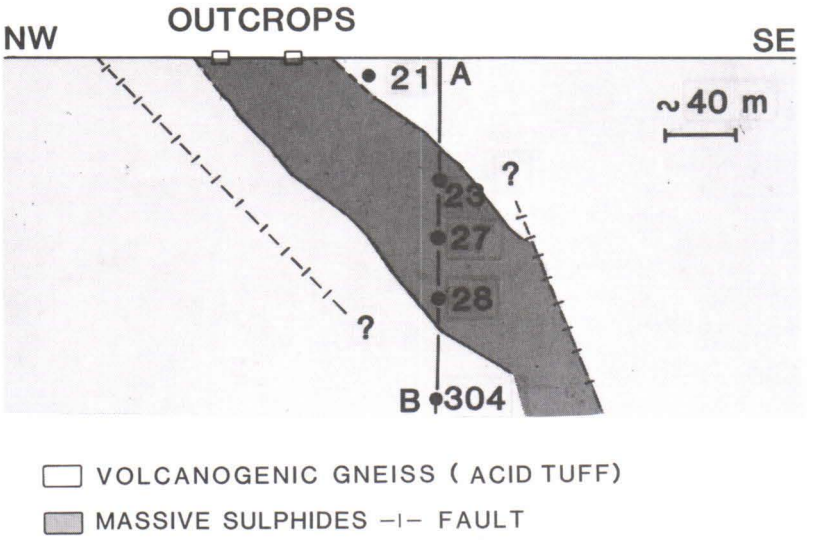

Fig. 3. Schema of location of sampled drill cores in the inclined ore-bearing stratum (a cross section), Kangasjärvi. The A-B line is shown also in Fig. 6.

RESULTS

The average P_2O_5 content for rhyolites is 0.13 %, for rhyodacite 0.17 %, for andesite 0.28 %, for tholeitic andesite 0.48 % and for basalts 0.16—0.56 % (Liebau and Koritnig 1970, 15-E-8). The means for altered and relatively unaltered volcanogenic gneisses hosting the Kangasjärvi deposit are presented in Table 1. The contents of P_2O_5 for intermediate and mafic rocks correspond reasonably well with the literature values but the mean content for felsic gneisses is markedly lower. A low content of P_2O_5 seems to be characteristic for the felsic, fine-grained quartz-feldspar gneisses, interpreted as metamorphic derivatives of acidic tuffs, also in other parts of the Pielavesi-Pyhäsalmi area (Huhtala 1979).

Transverse distributions of P_2O_5 and sulphur in a vertical profile are shown in Fig. 4. P_2O_5 contents are very low in various rocks adjacent to the deposit. Relatively low contents are encountered both for garnet-cordierite-anthophyllite gneisses and for garnet-cordierite-sillimanite gneisses. The distribution of P_2O_5 is approximately inverse to the distribution of sulphur particularly in d.d. cores 21, 23 and 27. The alteration in the host rocks is depicted in Fig. 5 in terms of indices K_2O/Na_2O and $(MgO+K_2O)/(MgO+K_2O+Na_2O+CaO)$ adopted from Hashimoto (1977). The alteration shown by the four element index and the distribution pattern of sulphur seem to be fairly similar. Their widths, however, although they are considerably larger than the halos of K_2O/Na_2O, are less than 100 m.

The distributions of FeO_{tot}, P_2O_5 and S in drill core 27 are presented together with pyrite sulphur isotopic variation in Fig. 6. No trend or systematic pattern in isotopic composition is observable in the hanging wall rocks. An increased variation in the $\delta^{34}S$ values is, however, noticeable in the altered rocks near the ore. The data show also a marked change in the isotopic composition under the massive sulphides. A shift from the maximum value of +8.1 ‰ to the minimum value of —13.7 ‰ occurs within the distance of a few metres. The average $\delta^{34}S$ value for the ore is 7.4 ‰ (see Table 2 for details), which is consistent with the values reported for pyrite of the Kuroko ores (cf. Lambert and Sato 1974).

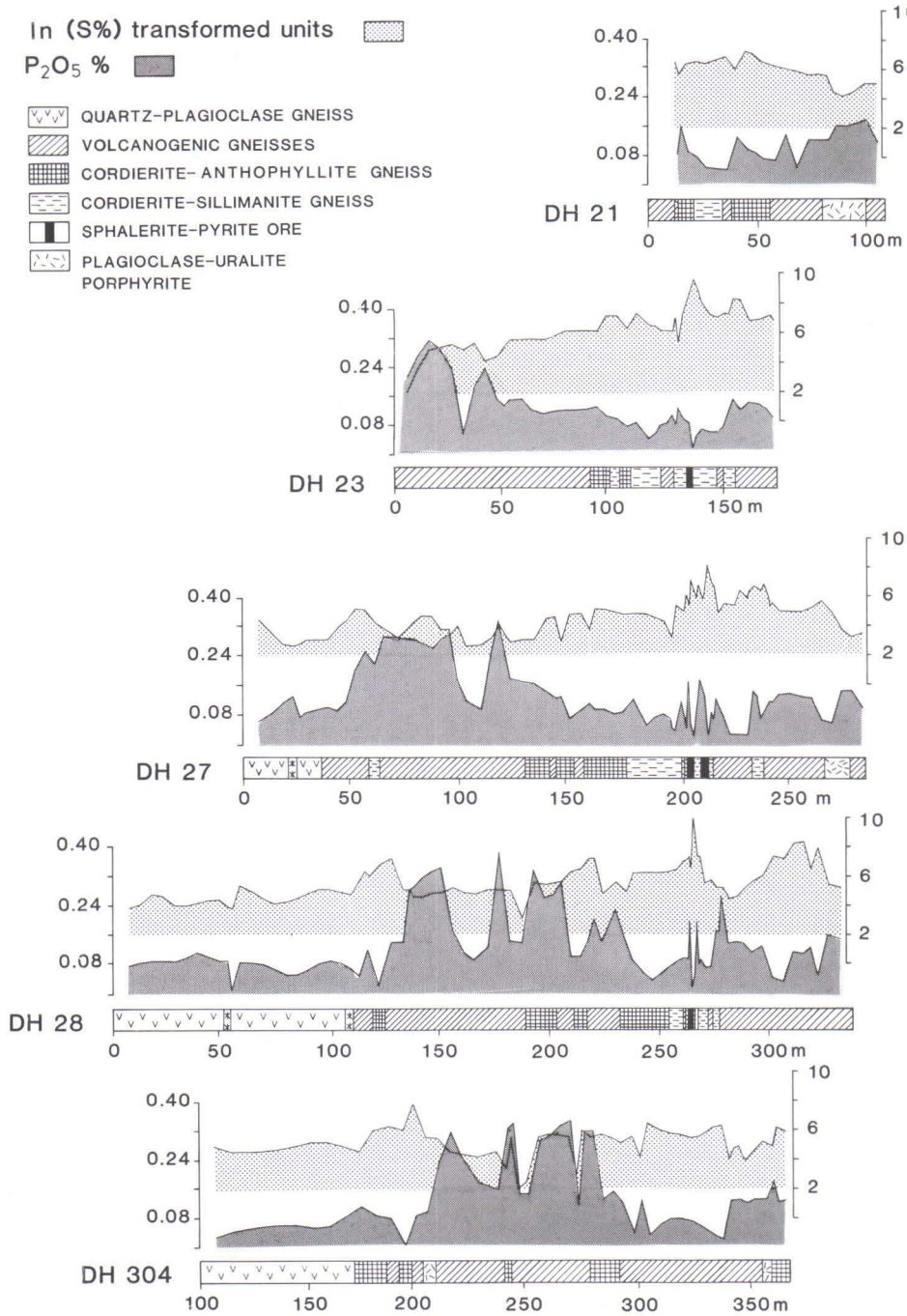

Fig. 4. Distributions of phosphorus and sulphur in a core profile cutting the ore-bearing strata, Kangasjärvi. Linear transformation between values 1 and 10 was computed for the natural logarithms of the S contents.

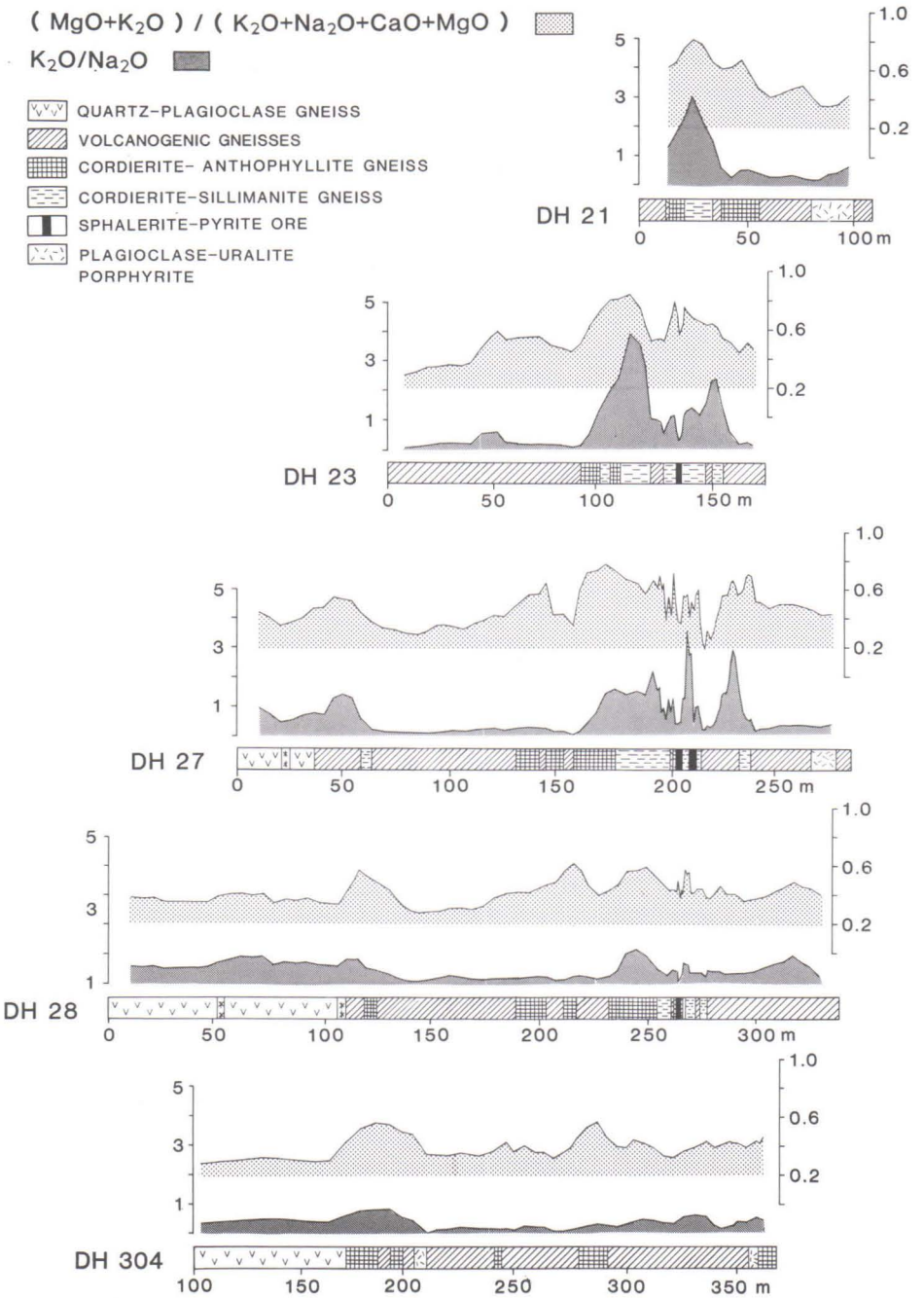

Fig. 5. Transverse distributions of the ratios K_2O / Na_2O and $(MgO + K_2O) / (MgO + K_2O + Na_2O + CaO)$ in the profile from the Kangasjärvi base metal deposit.

Table 1. Average contents of S and P_2O_5 in unaltered and altered volcanogenic gneisses around the Kangasjärvi deposit

Unaltered rocks: ratio of $(MgO + K_2O)/(MgO + K_2O + CaO + Na_2O) < 0.4$						
d.d. cores		21	23	27	28	304
Acid $SiO_2 > 66\%$						
	S %	0.37	0.43	0.99	0.73	0.20
	P_2O_5 %	0.05	0.07	0.07	0.06	0.07
	n	1	3	13	12	10
Intermediate $66\% > SiO_2 > 52\%$						
	S %	0.32	0.10	0.72	0.33	0.14
	P_2O_5 %	0.14	0.25	0.25	0.25	0.28
	n	6	6	18	22	17
Basic $SiO_2 < 52\%$						
	S %	0.24	0.52	0.73	0.24	0.08
	P_2O_5 %	0.14	0.13	0.14	0.14	0.14
	n	9	16	20	22	19

Altered rocks: ratio of $(MgO + K_2O)/(MgO + K_2O + CaO + Na_2O) > 0.4$						
d.d. cores		21	23	27	28	304
Acid $SiO_2 > 66\%$						
	S %	0.99	1.16	2.45	1.43	0.37
	P_2O_5 %	0.05	0.07	0.03	0.05	0.05
	n	4	3	17	11	7
Intermediate $66\% > SiO_2 > 52\%$						
	S %	0.48	3.75	5.51	4.08	0.50
	P_2O_5 %	0.10	0.07	0.10	0.11	0.17
	n	7	11	18	9	4
Basic $SiO_2 < 52\%$						
	S %	1.48	3.11	3.39	0.89	1.32
	P_2O_5 %	0.10	0.10	0.11	0.10	0.10
	n	4	18	13	3	6

Table 2. Pyrite sulphur isotope compositions in diamond drill core 27, Kangasjärvi

DEPTH (m)	HOST ROCK	$\delta^{34}S$ ‰
41.50	volcanogenic gneiss, (intermediate)	6.6
42.40	”	2.2
45.50	”	1.0
53.80	”	— 2.7
66.50	”	— 0.3
136.30	cordierite-sillimanite gneiss	— 1.2
145.00	cordierite-anthophyllite gneiss	4.1
145.80	”	3.8
146.60	cordierite-anthophyllite gneiss	5.5
148.50	”	3.8
150.90	”	5.9
152.10	”	0.0
159.00	”	— 4.4
162.70	”	— 2.7
164.90	”	— 5.7
167.30	”	— 2.6
171.00	”	5.8
176.60	”	1.0
177.80	”	2.0
181.70	cordierite-sillimanite gneiss	— 6.7
184.60	”	3.7
188.25	”	5.0
190.70	”	1.9
194.40	”	1.5
194.70	”	— 6.3
195.20	”	— 6.1
195.80	”	— 2.0
196.60	”	4.8
197.40	”	7.2
198.20	”	3.3
200.40	”	5.5
201.30	”	7.5
201.70	pyrite-sphalerite ore	8.4
202.90	”	7.6
203.50	”	7.7
203.70	cordierite-sillimanite gneiss	— 0.7
204.60	”	— 1.4
206.50	”	0.4
207.70	”	0.4
207.90	pyrite-sphalerite ore	6.7
208.70	”	8.1
209.60	”	6.1
210.50	cordierite-sillimanite gneiss	5.9
213.50	volcanogenic gneiss, (felsic)	— 7.0
215.60	”	—13.7
215.85	”	—13.4
218.80	”	—11.0
221.60	”	— 6.1
222.90	”	— 5.2
226.00	”	— 7.6
228.20	”	—10.9
230.70	”	—13.2
232.10	cordierite-sillimanite gneiss	—10.6
233.70	”	—12.0
263.90	volcanogenic gneiss, (intermediate)	3.6
278.30	”	7.4
279.40	”	6.6

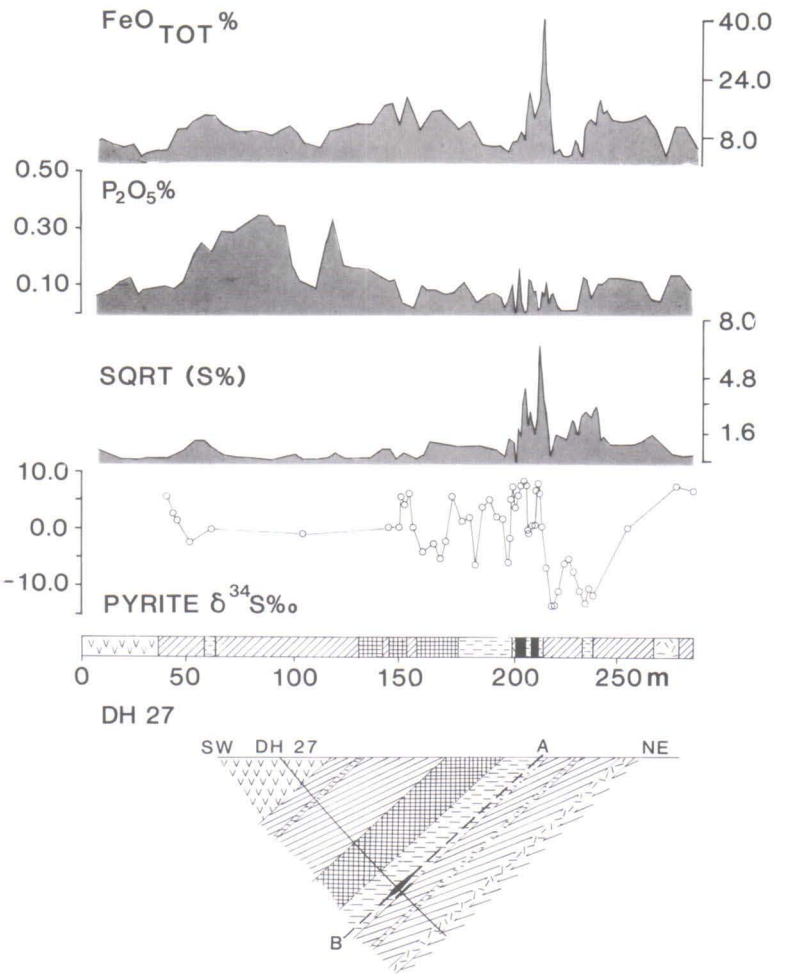

Fig. 6. Distributions of iron, phosphorus, sulphur and sulphur isotopes in d.d. core 27, Kangasjärvi. For the lithology see Fig. 4. SQRT = square root.

DISCUSSION

Transverse distribution of phosphourus

Apatite is known to be fairly insoluble in marine conditions. Even in solutions having pH values around 4 it is practically insoluble (Roberson 1966). The solubility is found to decrease with increase in temperature (Valyashko *et al.* 1968). Other factors affecting its distribution are total phosphorus concentration and concentrations of other major cations in the solution, salinity and the Mg/Ca ratio (Atlas 1976). A high Mg/Ca ratio inhibits phosphate precipitation (Martens and Harris 1970). The pH value in the solution is, however, considered to be the major factor determining the phosphate equilibrium. Gulbrandsen (1969) has shown that apatite precipitation in sea water is strongly dependent on pH: the lower the pH the larger amount of phosphate dissolved in the solution.

The results obtained from the host rocks of the Kangasjärvi base metal deposit show that part of the primordial P_2O_5 bound in the altered rocks is lost to the fluid (Figs. 4 and 6, Table 1). The correlation coefficients between P_2O_5, ln(S) and the alteration index $(MgO + K_2O) / (MgO + K_2O + CaO + Na_2O)$ in the volcanogenic rocks are shown in Table 3. Particularly the change in the correlation between P_2O_5 and ln(S) is systematic,

indicating that in the upper part of the massive sulphides acid altering fluids have prevented phosphate precipitation and caused leaching of phosphorus from the sediments. Partial leaching of phosphorus explains also the negative transverse halo-type pattern and its inverseness to the patterns of sulphur and the alteration index (Figs 4 and 5). Melson (1973) has shown using an electron microprobe that palagonized basaltic glass may be depleted in phosphorus in sea floor environment. It is suggested then that part of the phosphorus incorporated in the volcanogenic sediments at Kangasjärvi was originally bound not in crystalline phosphates but in glassy material. According to Huhtala (1979) the alteration in the Pyhäsalmi-Säviä district is characterized by depletion in the contents of Na and Ca, and increase in the contents of Mg, Fe and Al. Similar or closely related alteration has been reported for the host rocks of many massive stratiform base metal deposits of Precambrian age (Govett 1983, 249—328). This suggests that the leaching of phosphorus is closely connected to the host rock alteration and to the introduction of ore forming fluids.

Table 3. Correlation coefficients of P_2O_5, ln(S) and alteration index $(MgO + K_2O)(MgO + K_2O + CaO + Na_2O)$ in volcanogenic rocks, diamond drill cores 21, 23, 27, 28 and 304, Kangasjärvi

d.d. core	samples	Ind/P_2O_5	Ind/ln(S)	P_2O_5/ln(S)
21	31	—0.77	0.62	—0.70
23	61	—0.61	0.53	—0.57
27	103	—0.50	0.56	—0.52
28	80	—0.60	0.44	—0.37
304	63	—0.61	0.58	—0.20

Transverse distribution of pyrite $\delta^{34}S$

Two distinct features characterize the pyrite $\delta^{34}S$ pattern (Fig. 6): increased variation in the altered hanging wall rocks and a sharp shift from the average value of +7 ‰ in the massive ore to the average value of —13 ‰ in the rocks underlying it.

Amphibolite facies metamorphic processes tend to dissolve, decompose and remobilize sulphur compounds and thereby cause local changes in isotopic compositions. Metamorphic mobilization and redistribution has been demonstrated for instance by Rye and Rye (1974). It would, however, seem unlikely that these phenomena are sufficient to account for the isotopic variations observed. Variation may also be attributed to slight changes in pH and/or f_{O_2} of the fluid (cf. Mäkelä 1977). Furthermore, Andrews (1979) has found considerable remobilization of S in deep ocean floor basalts during low-temperature basalt/sea water interaction, resulting in formation of secondary pyrite and a bulk loss of 50 to 60 % of the primordial sulphur content. He suggested that unstable oxidised sulphur species and generation of SO_4^{2-} ion may explain the highly variable $\delta^{34}S$ values which characterize secondary sulphides in oceanic crust. The increase in the variation of sulphur isotopic composition in the most altered rocks in the volcanogenic succession at Kangasjärvi (Fig. 6) implies the involvement of similar or closely related processes.

The shift from $\delta^{34}S$ values of +7 ‰ to —13 ‰ within the space of a few metres suggests an abrupt change in the f_{O_2} of the fluid causing sulphur to precipitate both as sulphate and as sulphide (cf. Ohmoto 1972). This interpretation is supported by barium (barite) contents up to the level of 0.4 % BaO compared with the halo level of 0.1 %. Similar lightening in the sulphur isotopic composition with stratigraphic height in a hematite-quartz-barite zone is found in the Shakanai deposit, Japan (Kajiwara 1971).

Enrichment of phosphorus and sulphur in a distal environment at Vihanti, Finland: a comparison

The results show that sulphur in the volcanogenic rocks hosting the massive sulphides at Kangasjärvi is enriched in altered rocks and that the content of P_2O_5 is at the level encountered for volcanogenic rocks or even lower. At Vihanti, Finland, in the volcanic-sedimentary host rocks of the Lampinsaari Zn-Cu-Pb ore complex, phosphate enrichment

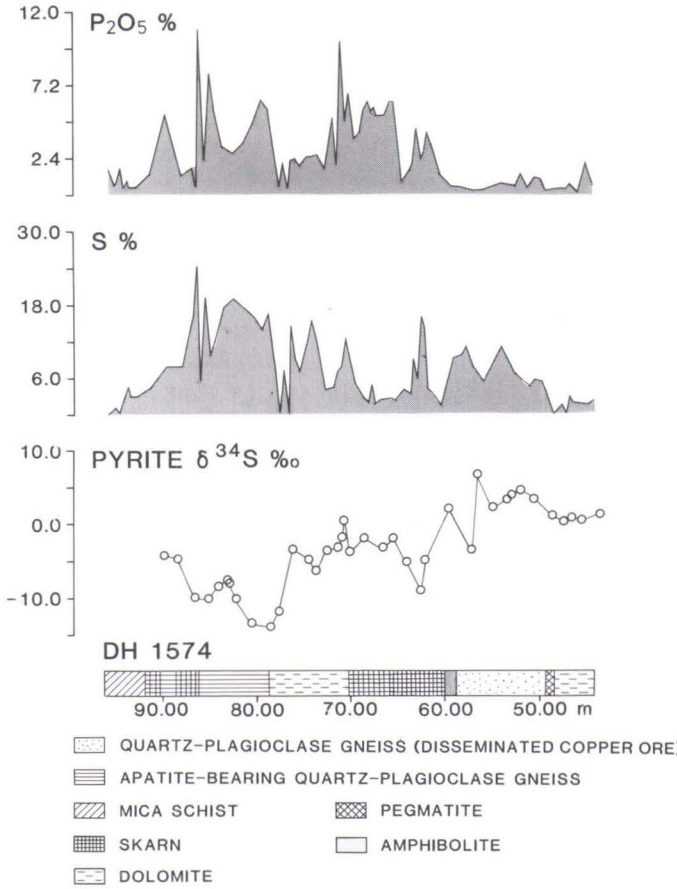

Fig. 7. Distributions of phosphorus, sulphur and sulphur isotopes in d.d. core 1574, Lampinsaari ore deposit, Vihanti. For further details see Rehtijärvi *et al.* (1979).

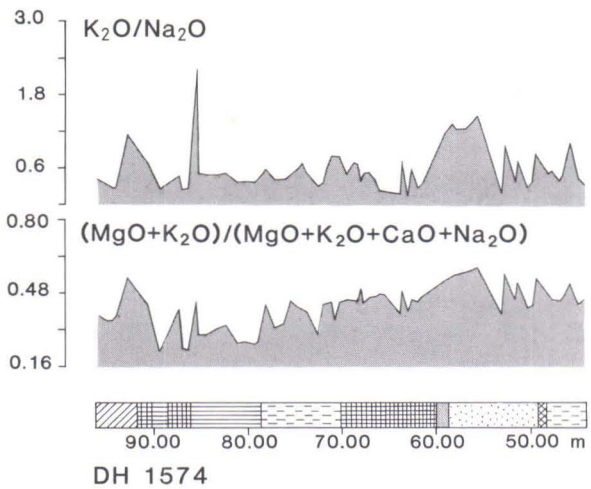

Fig. 8. Tranverse distributions of the ratios K_2O and $(MgO + K_2O)/(MgO + K_2O + Na_2O + CaO)$ in diamond drill core 1574, Lampinsaari ore deposit, Vihanti. For the lithology see Fig. 7.

(Fig. 7) is found to characterize the lithological units in the hanging wall (Rehtijärvi *et al.* 1979, Rauhamäki *et al.* 1980). Fine-grained quartz-plagioclase gneisses are interpreted as metamorphic derivatives of felsic tuffs. In the gneiss stratigraphically below the phosphatic dolomite, U, Fe and S are enriched together. Average contents are 20% S, 19.5% Fe_{tot} 3.2% P_2O_5 and 248 ppm U in the pyrite-banded variant of the apatite-bearing quartz-plagioclase gneiss (Rehtijärvi *et al.* 1979).

The ratio K_2O/Na_2O is at the same level in the different rock types as in the drill core 1574 (Fig. 8). Noticeable increase is observed only in quartz-plagioclase gneiss hosting the disseminated copper ore. It would thus seem reasonable to attribute the observed increase to hydrothermal activity, probably genetically related to copper introduction. Since the pyritic ore of the sc. uranium-apatite horizon does not show marked alteration it may be deduced that this unit deposited away from the hydrothermal centre, in a distal environment where normal marine sedimentary conditions prevailed. It is also possible, though not likely, that the pyrite-pyrrhotite assemblage of the uranium- and apatite-bearing horizon has only a spatial relation to the Lampinsaari ores proper.

Contrary to the distribution of K_2O/Na_2O in the rock sequence overlying the ore-bearing strata, the alteration index $(MgO + K_2O)/(MgO + K_2O + CaO + Na_2O)$ seems to increase towards the disseminated copper ore (Fig. 8). On the basis of an earlier interpretation of changes in lithology and in sulphur isotopic composition of sulphides (Rehtijärvi *et al.* 1979), the MgO/CaO ratio is largely expected to reflect the sequential changes of pH in the sea water. On this view, the trend shown by the four element alteration index would also indicate changing depositional conditions in addition to alteration, particularly in a distal environment having restricted sea water circulation.

CONCLUDING REMARKS

The pattern and the related negative halo-type distribution shown by P_2O_5 in the volcanogenic rocks hosting the Kangasjärvi base metal deposit are attributed both to former variation in volcanogenic rocks and to partial leaching of phosphorus in processes closely related to hydrothermal alteration and ore formation. The halo is restricted in transverse direction to less than 100 m and is comparable to the halos of alteration indices computed using normalized contents of large ion lithophile elements. The negative correlation of P_2O_5 to sulphur content is strongest near the upper part of the massive sulphide layer and considered to indicate the direction of introduction of acid altering fluids.

The increased variation in the $\delta^{34}S$ values in the hanging wall rocks may likewise be attributed to processes related to alteration. The sharp shift in pyrite sulphur isotope composition marks a transition to the stratigraphic unit that deposited after the massive ore. The shift from $\delta^{34}S$ average values of +7‰ to average values of —13‰ is interpreted to imply a temporary change in the depositional conditions and may indicate a stratigraphic height where sulphate coprecipitation with sulphide was increased. Such an interpretation would be in accordance with the zonation found to characterize Kuroko-type massive sulphide ores.

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REFERENCES

Andrews, A.J., 1979. On the effect of low-temperature seawater-basalt interaction on the distribution of S in oceanic crust, layer 2. Earth Planet. Sci. Lett., 46, 68—80.

Atlas, E.L., 1976. Phosphate equilibria in seawater and interstitial waters. Ph.D. thesis, Oregon State University, 154 p.

Doe, B.R. & Zartman, R.E., 1979. Plumbotectonics. The Phanerozoic, 22—70, in Geochemistry of hydrothermal ore deposits, ed. H.L. Barnes, John Wiley and Sons, New York.

Govett, G.J.S., 1983. Rock geochemistry in mineral exploration. vol 3, in Handbook of exploration geochemistry, ed. G.J.S. Govett, Elsevier, Amsterdam, Oxford, New York, 461 p

Gulbrandsen, R.A., 1969. Physical and chemical factors in the formation of marine apatite. Econ. Geol., 64, 365—382.

Hashimoto, K., 1977. The Kuroko deposits of Japan and exploration strategies. XII Convencion National AIMMGM, Asociation de Ingenieros de Minas Metalurgistas Y Geologos de Mexico. Acapulco.

Helovuori, O., 1979. Geology of the Pyhäsalmi ore deposit, Finland. Econ. Geol., 74, 1084—1101.

Huhtala, T., 1979. The geology and zinc-copper deposits of the Pyhäsalmi-Pielavesi district, Finland. Econ. Geol., 74, 1069—1083.

Kahma, A., 1973. The main metallogenic features of Finland. Geol. Surv. Finland Bull., 265, 28 p.

Kahma, A., Saltikoff, B. & Lindberg, E., 1976. Ore deposits of Finland, Map 1:1000.000, Geological Survey of Finland.

Kajiwara, Y., 1971. Sulfur isotope study of the Kuroko-ores of the Shakanai No. 1 deposit, Akita Prefecture, Japan. Geochem. J., 4, 157—181.

Lambert, I.B. & Sato, T., 1974. The Kuroko and associated ore deposits of Japan: A review of their features and metallogenesis. Econ. Geol., 69, 1215—1236.

Liebau, F. & Koritnig, S., 1970. Phosphorus in Handbook of Geochemistry, II/2, ed. K.H. Wedepohl, Springer Verlag, Berlin, Heidelberg, New York.

Mäkelä, M., 1977. Sulfur isotope stratigraphy in some Finnish ore deposits. Geol. För. Stockholm Förh., 99, 163—171.

Mäkelä, M. & Tammenmaa, J., 1977. A system for precise sulphur isotope analysis by a small mass spectrometer. Geol. Surv. Finland, Rep. of Investigation, 20, 23 p.

Martens, C.S. & Harris, R.C., 1970. Inhibition of apatite precipitation in marine environment by magnesium ions. Geochim. Cosmochim. Acta, 34, 621—625.

Melson, W.G., 1973. Basaltic glasses from the Deep Sea Drilling Project: chemical characteristics, compositions of altered products, and fission track "ages". EOS Trans. Amer. Geophys. Union, 54, 1011—1014.

Ohmoto, H., 1972. Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. Econ. Geol., 67, 551—578.

Plimer, I.R., 1978. Proximal and distal strata-bound ore deposits. Mineral. Deposita, 13, 345—353.

Rauhamäki, E., Mäkelä, T. & Isomäki, O-P., 1980. Geology of the Vihanti mine, 12—24, in Precambrian ores of Finland. Guide to excursions 078 A + C, part 2 (Finland), ed. T.A. Häkli, 26. International Geological Congress, Paris, 1980. Geol. Surv., Finland.

Rehtijärvi, P., Äikäs, O. & Mäkelä, M., 1979. A middle Precambrian uranium- and apatite-bearing horizon associated with the Vihanti zinc ore deposits, western Finland. Econ. Geol., 74, 1102—1117.

Roberson, C., 1966. Solubility implications of apatite in sea water. U.S. Geol. Surv. Prof. Paper 550-D, 178—185.

Rye, D.M. & Rye, R.O., 1974. Homestake gold mine, South Dakota: I., Stable isotope studies. Econ. Geol., 69, 293—317.

Salli, I., 1983. Pielaveden kartta-alueen kallioperä — Pre-Quaternary rocks of the Pielavesi map-sheet area. Geological map of Finland 1:100 000, sheet 3314, Geol. Surv. Finland, 29 p.

Simonen, A., 1980. The Precambrian of Finland. Geol. Surv. Finland Bull., 304, 58 p.

Stacey, J.S. Doe, B.R., Silver, L.T. & Zartman, R.E., 1977. Plumbotectonics IIA, in Precambrian massive sulfide deposits. Geochronology and problems of the metallogeny, Nauka, Moscow, 93—106 (in Russian).

Vaasjoki, M., 1981. The lead isotopic composition of some Finnish galenas. Geol. Surv. Finland Bull., 316, 30 p.

Valyashko, V.M., Kogarko, L.N. & Khodakovskiy, L.L., 1968. Stability of fluorapatite, chlorapatite and hydroxylapatite in aqueous solutions at different temperatures. Geochem. Internat., 5, 21—30.

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