An Application of Lithogeochemistry to the Evaluation of the Ni-sulphide Ore Potential of Weathered Serpentinites in the Fortaleza de Minas Greenstone Belt, Minas Gerais, Brazil

JAAP OOSTINDIËR[1,+], PAUL M. TAUFEN[2,*] and SIMON P. VRIEND[1]

[1] *Vening Meinesz Laboratory, Department of Geochemistry, Institute of Earth Sciences, University of Utrecht, P.O. Box 80.021, 3508 TA Utrecht, The Netherlands*
[2] *B.P. Mineração LTDA, Rua Martins Ferreira 91, Botafogo, Rio de Janeiro RJ, Brazil*

ABSTRACT

Oostindiër, J., Taufen, P.M. and Vriend, S.P., 1988. An application of lithogeochemistry to the evaluation of the Ni-sulphide ore potential of weathered serpentinites in the Fortaleza de Minas greenstone belt, Minas Gerais, Brazil. *J. Geochem. Explor.*, 31: 57–73.

A practical application of lithogeochemistry to the classification of weathered serpentinites as to whether or not serpentinites are host rocks to Ni-sulphide ore is presented. An effort is made to apply existing concepts used to distinguish between fertile and sterile unweathered ultramafics to explain the observed chemical differences between fertile and sterile weathered serpentinites in southwestern Minas Gerais, Brazil.

The data comprise total-attack chemical analyses for Al, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Si, Ti, V, and partial-attack determinations of Cu and Ni as ascorbic acid, hydrogen peroxide-soluble metal. Student's t-tests are used to identify element concentration differences between the two serpentinite groups. Discriminant analysis is used to classify the weathered fertile and sterile serpentinites. Non-linear mapping and fuzzy c-means clustering help to assess the validity of the discriminant analysis. Finally, chemical element associations provide extra information on geological and mineralogical causes that can be responsible for the identified differences.

It is found that a clear separation and classification of weathered serpentinites is possible using the procedures presented. The observed chemical differences between fertile and sterile serpentinites are interpreted in terms of original magmatic differentiation, the degree of sulphur saturation of the original magma and the behavior of the derived ultramafic rocks in a tropical weathering environment.

[+] Present address: Shell Internationale Petroleum Maatschappy. B.V., Postbus 162, 2501 AN Den Haag, The Netherlands.
[*] Present address: W.M.C. Mineração LTDA, Rua Sernambetiba 4462, Barra da Tijuca, Rio de Janeiro RJ, Brazil.

INTRODUCTION

Geochemical exploration for Ni-sulphides in ultramafic rocks has been focused traditionally on the positive identification of weathered sulphides or gossans, or on the chemical characterization of fresh ultramafic igneous rock hosting Ni-sulphide mineralization. The identification of weathered massive or disseminated Ni-sulphides is generally not fraught with difficulty in modern geochemical exploration, due to past extensive studies (Bull and Mazzucchelli, 1975; Wilmshurst, 1975; Moeskops, 1977).

The identification of ultramafic volcanics hosting massive sulphide deposits and their discrimination from sterile ultramafic volcanics has been studied in unweathered ultramafic rocks. Several discriminating criteria have been developed for unweathered mineralization-bearing (fertile) ultramafic rocks, including Ni, Cu, Co, and S enrichment of ultramafics in sulphide-selective leaches (Cameron et al., 1971), MgO enrichment in the fertile basal flows within ultramafic volcanic piles (Groves et al., 1979; Naldrett et al., 1984), and Ni-depletion in olivines of ultramafic volcanics due to Ni-partitioning between immiscible sulphide and silicate melts (Duke, 1979; Fleet and MacRae, 1983; Naldrett et al., 1984).

Relatively few information has been published, however, regarding the discrimination between chemically weathered, fertile (Ni-sulphide-bearing) ultramafics or serpentinites and their weathered sterile equivalents. In weathered rocks, discrimination using sulphide-selective leaches is complicated by the already leached state of the ultramafics. Furthermore, the use of MgO-enrichments is not possible due to the solubility of MgO in the surficial environments of strong chemical weathering. Subsequently, possible Ni-depletion in ultramafic silicates, indicative of fertile host rocks, is difficult to quantify without knowledge of the original MgO content of the rock.

We present here an application of what is known about the relationship between fertile volcanics and their contained massive Ni-sulphide in fresh rocks in order to discriminate weathered fertile from weathered sterile serpentinites in the humid, tropical environment of southwestern Minas Gerais, Brazil. In this approach, several distinguishing features of fertile, Ni-sulphide ore-hosting, ultramafics and sterile ultramafics are considered. Magmatic differentiation leading to more MgO-rich basal, ore-hosting ultramafics versus other volcanics stratigraphically higher in the volcanic pile (Groves et al., 1979; Naldrett et al., 1984) is thought to be important. The saturation with respect to sulphide, sulphur of magmas which separate immiscible Ni-sulphides (Buchanan and Nolan, 1979; Campbell et al., 1979) is likewise considered to be important. In addition, the partitioning of Ni and Cu between silicates and sulphides in the solidifying magma (Häkli, 1963; Duke, 1979; Naldrett et al., 1984) is held to be critical in assessing potential ultramafic ore hosts.

To test the possibility of classifying fertile and sterile weathered serpentin-

ites in the Fortaleza de Minas greenstone belt, the O'Toole Ni-sulphide ore-hosting serpentinite was sampled along with nearby serpentinites barren with respect to Ni-sulphides. Ascorbic acid, hydrogen-peroxide cold leach (Cameron et al., 1971; Lynch, 1971) and total-metal determinations were used to evaluate the fertile or sterile nature of the serpentinites. In the work presented here, Student's t-tests are used to determine whether real differences in element concentrations exist between the two serpentinite groups and discrimination analysis is utilized to optimize group separation. Nonlinear mapping and fuzzy c-means clustering give a more general appraisal of the multivariate data structure which helps to check the validity of the discriminant function. Correlation coefficients of the chemical variables are used to help offer a geological and mineralogical explanation of the observed differences in element concentrations between fertile and sterile serpentinites.

GEOGRAPHICAL, GEOLOGICAL AND CLIMATIC SETTING

The Fortaleza de Minas greenstone belt is part of the late Archaean Furnas region of granitoid-greenstone terrain in Minas Gerais, Brazil. It occurs as a northwest-trending, 2-km-wide volcano-sedimentary sequence with felsic gneiss of the regional basement complex exposed to the northeast and southwest. The volcano-sedimentary sequence comprises metamorphosed ultramafic flows with locally preserved spinifex texture, komatiitic- and tholeiitic metabasalts, metatuffs and metasediments including ferruginous cherts (Teixeira and Danni, 1975). The belt is polydeformed, has undergone a lower amphibolite metamorphosis (J.T. Cheney, pers. commun., 1985), and exhibits little preservation of primary igneous mineralogy and texture. The ultramafic and mafic rocks can be mineralogically separated in three major groups: serpentinites, clinopyroxenites and amphibolites (J.T. Cheney, pers. commun., 1985).

Stratigraphically several ultramafic-mafic volcanic cycles are recognized. A complete cycle consists, from base to top, of serpentinite, talc-carbonate rock, sphene-chlorite-tremolite pyroxenites, sphene-chlorite-actinolite amphibolites, plagioclase-hornblende amphibolites and metasediments, frequently developed as ferruginous chert (J.T. Cheney, pers. commun., 1985; Spray, 1985).

One such cycle hosts the O'Toole Ni-Cu-Co sulphide deposit. The orebody and associated serpentinites are located about 5 km southeast of the town of Fortaleza de Minas in southwestern Minas Gerais. The deposit contains 5.3 million tons of ore, grading 2.6% Ni, 0.4% Cu, 0.05% Co and 1.1 g/t combined platinum group elements. The orebody extends 1.6 km along strike, has a prevailing true thickness from 2 to 10 m and attains a depth of at least 500 m. Fresh ore comprises mainly pentlandite and pyrrhotite with minor chalcopyrite and cobaltite. The deposit crops out as a weathered gossan. A simplified
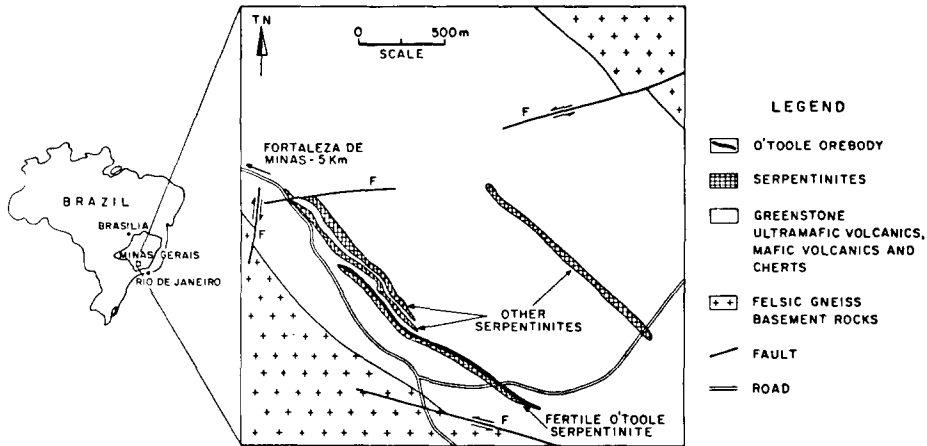
Fig. 1. Serpentinite exposures in the vicinity of the Fortaleza de Minas O'Toole nickel sulphide deposit, Minas Gerais, Brazil.

geological map, showing the ore deposit and the fertile and barren serpentinites sampled in this study, is presented in Fig 1.

The region around the Fortaleza de Minas O'Toole deposit falls within the Minas Gerais Southern Plateau morphological and structural province. Its climate is humid tropical with a dry season from June to August and a rainy season from December to February. Rainfall averages 1600 mm per year. The mean annual temperature is 19°C with usual maxima and minima of 35°C and 0°C respectively. The area is covered by a mixture of scrub vegetation and deciduous forest with a large portion of the land devoted to crop raising and pasture (Galvão, 1977).

SAMPLING AND ANALYTICAL PROCEDURES

A total of 55 serpentinite rock samples was collected from the freshest outcrops available. No fresh sulphides were detected in any of the samples. Samples were 1–2 kg chip composites. Sets of duplicate samples were collected to monitor sample reproducibility. Samples were crushed in a steel jawcrusher and pulverized to minus 200 mesh in a steel disc mill. Quartz blanks were used to check for any sample contamination.

Al, Ca, Cr, Fe, Mg, Mn, Si, Ti and V were determined by ICP analysis after sample digestion using a sodium hydroxide fusion method. Total Cu and total Ni were determined by AAS after a hot $HF-HNO_3-HClO_4$ acid digestion. Soluble Cu and soluble Ni were determined by AAS using an ascorbic acid, hydrogen peroxide cold leach after Lynch (1971) and Cameron et al. (1971).

Duplicate field samples showed a satisfactory sample representativity. Quartz blanks were found to contain minor contamination of Mg and Fe (0.05 and

0.10% respectively). These concentrations are of no importance in relation to serpentinite sample concentrations. Laboratory and international standards were used to check ICP performance. Measured concentrations in standards were found to closely match standard reference concentrations. Precision as observed from relative standard deviations from duplicate analyses are about 5% for all elements except for soluble Cu for which a precision of 17% was calculated.

DATA DESCRIPTION

Analyses of the 55 rock samples are given in Table 1 where samples are grouped as fertile or sterile, based on their known association or lack thereof with Ni-sulphide mineralization. In these analyses, ascorbic acid, hydrogen-peroxide leach concentrations of Cu and Ni are designated as soluble metal in the serpentinites. Leach concentrations were subtracted from total metal analyses to give calculated residual Cu and Ni concentrations. These residual concentrations are considered to represent silicate-bound Cu and Ni in the serpentinites.

The Ca, Cr, total Ni, soluble Ni, residual Ni, total Cu, soluble Cu and residual Cu data approximate a log-normal distribution. These variables were log-transformed prior to further analysis. Histograms of the variables listed in Table 1 are given in Fig. 2. The fertile and sterile sample groups are indicated in the histograms.

T-TESTS

To test the significance of differences between mean element concentrations in fertile and sterile serpentinites, t-tests were undertaken. In Table 2 mean and standard deviations of the fertile and sterile groups are given as well as t-statistics and two-sided probabilities. The results of the t-tests indicate that there is a very high probability (significance level 0.001) that the Mn, Ca, Cr, V and residual Cu contents of fertile and sterile groups have different population means. At the 0.05 significance level the Fe, total Ni and total Cu contents of fertile and sterile groups also have different population means. Thus indicating significant differences between the ore hosting serpentinite and barren serpentinites for these determinations.

DISCRIMINANT ANALYSIS

Linear discriminant functions have been used, among others, by Govett (1972) in a lithogeochemical study of sulphide hosting pillow lavas and basalts and by Bull and Mazzucchelli (1975) in the evaluation of gossans. To optimize serpentinite classification in terms of fertile and sterile flows based on differ-

TABLE 1

Chemical analyses of weathered serpentinite rock samples

Fertile group

Sample no.	Si (%)	Ti (%)	Al (%)	Fe (%)	Mn (%)	Mg (%)	Ca (%)	Cr (ppm)	V (ppm)	Ni_{TOT}* (ppm)	Ni_{SOL}* (ppm)	Ni_{RES}* (ppm)	Cu_{TOT}* (ppm)	Cu_{SOL}* (ppm)	Cu_{RES}* (ppm)
JCGR 430	17.7	0.16	1.03	8.2	0.10	20.5	0.02	4142	66	1760	390	1370	94	49	45
JCGR 431	17.3	0.18	1.20	8.9	0.11	20.5	0.02	5767	77	1700	430	1270	710	385	325
JCGR 432	16.8	0.21	1.32	8.6	0.15	19.9	0.02	7496	93	1980	380	1600	290	126	164
JCGR 433	17.1	0.20	1.42	8.3	0.08	19.8	0.02	6539	77	1940	410	1530	37	12	25
JCGR 434	18.5	0.20	1.27	9.3	0.10	19.5	0.02	5980	85	1950	410	1540	22	4	18
JCGR 435	17.2	0.16	1.02	8.7	0.13	21.4	0.02	5588	69	2480	410	2070	14	3	11
JCGR 436	16.7	0.21	1.26	9.5	0.17	18.7	0.02	8180	88	1500	340	1160	160	50	110
JOIR 1	18.1	0.21	1.16	9.1	0.11	20.6	0.07	5561	86	3150	690	2460	48	19	29
JOIR 2	18.4	0.25	1.25	8.3	0.11	20.2	0.23	6207	86	4100	745	3355	48	13	35
JOIR 3	19.3	0.24	1.40	8.9	0.12	20.6	0.02	6480	82	2400	415	1985	62	23	39
JOIR 4	18.2	0.21	1.33	8.7	0.12	19.6	0.02	6085	71	2250	400	1850	62	20	42
JOIR 5	18.6	0.19	1.09	9.0	0.12	21.7	0.02	5916	69	2600	475	2125	32	10	22
JOIR 6	18.8	0.20	1.13	9.1	0.12	22.1	0.02	6007	69	2500	480	2020	32	11	21
JOIR 7	18.7	0.21	1.23	9.7	0.12	21.5	0.02	6072	83	2350	440	1910	164	45	119
JOIR 8	18.3	0.21	1.22	9.2	0.12	21.3	0.02	5872	81	2500	575	1925	110	37	73
JOIR 9	18.4	0.15	0.80	11.1	0.15	20.2	0.02	3736	78	3150	820	2330	80	32	48
JOIR 10	18.6	0.14	0.78	11.4	0.16	20.6	0.02	3792	79	3150	850	2300	78	29	49
JOIR 11	18.8	0.22	1.21	8.8	0.11	21.4	0.18	5792	77	3950	805	3145	52	17	35
JOIR 12	19.6	0.23	1.36	8.6	0.13	20.7	0.02	6291	77	2250	360	1890	102	33	69
JOIR 13	18.5	0.17	0.90	10.2	0.12	21.3	0.02	5398	76	1950	435	1515	162	87	75
JOIR 14	18.9	0.18	0.95	10.3	0.13	21.9	0.02	5497	78	2000	470	1530	216	115	101
JOIR 15	19.4	0.23	1.35	10.9	0.11	20.5	0.02	6393	93	1900	410	1490	24	8	16
JOIR 37	19.2	0.19	1.09	9.9	0.12	21.6	0.02	6316	80	2500	600	1900	58	22	36
JOIR 38	19.3	0.19	1.12	9.7	0.11	21.6	0.02	5970	78	2800	615	2185	40	13	27
JOIR 39	19.1	0.20	1.27	8.7	0.13	22.4	0.02	6302	71	2250	470	1780	34	9	25
JOIR 40	19.0	0.24	1.27	9.8	0.13	21.7	0.02	6495	84	2450	505	1945	64	18	46
JOIR 41	18.9	0.21	1.22	9.6	0.13	21.3	0.02	6252	85	2700	525	2175	82	23	59
Minimum:	16.7	0.14	0.78	8.2	0.08	18.7	0.02	3736	66	1500	340	1160	14	3	11
Maximum:	19.6	0.25	1.42	11.4	0.17	22.4	0.23	8180	93	4100	850	3355	710	385	325

Sterile group

Sample no.	Si (%)	Ti (%)	Al (%)	Fe (%)	Mn (%)	Mg (%)	Ca (%)	Cr (ppm)	V (ppm)	Ni_{TOT}* (ppm)	Ni_{SOL}* (ppm)	Ni_{RES}* (ppm)	Cu_{TOT}* (ppm)	Cu_{SOL}* (ppm)	Cu_{RES}* (ppm)
JCGR 437	16.7	0.20	1.35	10.1	0.11	17.5	1.86	3844	69	1900	810	1090	135	102	33
JCGR 438	17.3	0.14	1.03	6.8	0.04	21.9	0.02	3168	53	2950	370	2580	12	4	8
JCGR 440	16.6	0.18	1.09	8.5	0.13	19.8	1.39	4253	79	3180	510	2670	4	2	2
JCGR 441	17.9	0.15	0.93	7.7	0.16	21.0	0.52	4272	58	2980	660	2320	14	7	7
JCGR 442	16.3	0.17	1.07	8.8	0.17	19.9	0.60	5778	65	2670	860	1810	305	262	43
JCGR 443	17.4	0.14	0.93	9.6	0.18	21.1	0.12	5675	61	3340	490	2850	17	9	8
JCGR 445	18.2	0.18	1.19	7.9	0.18	20.1	0.02	4477	67	3050	500	2550	77	26	51
JOIR 16	18.4	0.19	0.99	9.7	0.16	21.1	0.02	5752	68	2350	355	1995	172	115	57
JOIR 17	18.9	0.19	1.04	9.7	0.17	21.4	0.48	5397	77	2600	570	2030	196	155	41
JOIR 18	18.9	0.21	1.24	8.0	0.15	20.8	1.02	6437	66	2650	960	1690	20	18	2
JOIR 19	19.2	0.19	1.06	9.5	0.15	21.1	0.72	5298	79	2800	830	1970	244	250	1**
JOIR 20	18.7	0.18	1.06	9.6	0.15	20.7	0.83	4789	79	2850	885	1965	282	300	1**
JOIR 21	19.2	0.16	1.12	9.0	0.13	21.5	0.45	6300	77	2550	455	2095	20	10	10
JOIR 22	18.9	0.16	1.07	8.5	0.14	21.7	0.19	5994	69	2950	490	2460	16	10	6
JOIR 23	19.9	0.18	1.05	7.8	0.16	22.5	0.02	2849	64	2950	485	2465	8	5	3
JOIR 24	18.9	0.19	1.08	8.6	0.20	22.0	0.02	6239	73	2600	540	2060	44	24	20
JOIR 25	19.4	0.17	1.06	9.1	0.14	22.1	0.16	3092	67	2950	400	2550	8	4	4
JOIR 26	18.3	0.17	0.95	8.3	0.14	21.7	0.10	2840	59	2750	440	2310	12	7	5
JOIR 27	18.5	0.19	1.01	8.2	0.14	19.9	0.59	3129	67	2200	780	1420	20	9	11
JOIR 28	19.0	0.20	1.10	8.6	0.15	20.8	0.62	3069	71	2750	620	2130	10	7	3
JOIR 29	18.9	0.20	1.23	7.9	0.14	21.7	0.02	3142	61	1950	390	1560	16	8	8
JOIR 30	18.2	0.19	1.14	8.8	0.14	21.1	0.02	5909	68	2200	295	1905	12	7	5
JOIR 31	18.7	0.20	1.12	8.9	0.14	21.6	0.04	6534	69	2450	340	2110	12	6	6
JOIR 32	18.2	0.20	1.13	10.1	0.15	20.3	0.84	5026	81	2300	440	1860	32	8	24
JOIR 33	19.0	0.18	1.10	9.3	0.15	21.7	0.36	5261	73	2450	555	1895	12	6	6
JOIR 34	20.0	0.19	1.24	9.0	0.22	20.9	0.02	4729	85	2900	630	2270	96	50	46
JOIR 35	20.0	0.20	1.27	9.3	0.14	20.9	0.02	5153	80	3300	665	2635	168	84	84
JOIR 36	19.4	0.20	1.28	9.0	0.14	20.4	0.02	5141	75	3000	560	2440	80	38	42
Minimum:	16.3	0.14	1.03	6.8	0.04	17.5	0.02	2840	53	1900	295	1090	4	2	1
Maximum:	20.0	0.21	1.35	10.1	0.22	22.5	1.86	6534	85	3340	960	2850	305	300	84

*For Ni and Cu, tot, sol and res columns represent total, soluble and residual metal concentrations respectively. Ni and Cu, res columns are calculated values, subtracting soluble from total values.

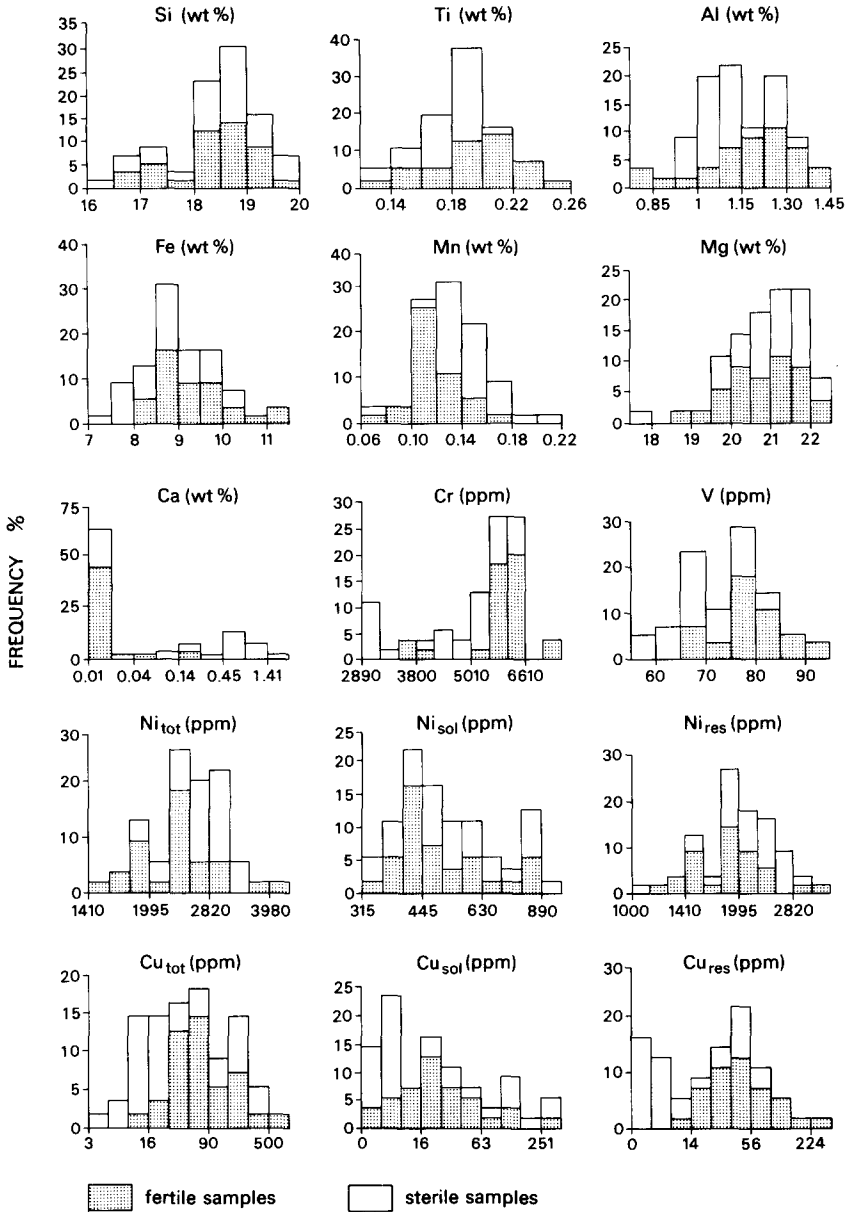**Negative values have been replaced by 1.

64

Fig. 2. Histograms of Si, Ti, Al, Fe, Mn, Mg, Ca, Cr, V, total Ni, soluble Ni, residual Ni, total Cu, soluble Cu and residual Cu. Data for Ca, Cr, total Ni, soluble Ni, residual Ni, total Cu, soluble Cu and residual Cu are log transformed.

ences observed in the t-tests, a discriminant analysis was run. Using a stepwise procedure, various combinations of elements were studied and it was found that a good discrimination was obtained with Fe, Mn, Ca, Cr, and V. The dis-

TABLE 2

T-tests on chemical variables of fertile and sterile serpentinites

Variable	fertile samples (27)		sterile samples (28)		t-tests	
	mean	standard deviation	mean	standard deviation	t statistic	two-tailed probability
Si	18.4	0.81	18.5	0.97	−0.47	0.639
Ti	0.20	0.028	0.18	0.019	2.74	0.009
Al	1.17	0.17	1.10	0.11	1.75	0.087
Fe	9.35	0.86	8.80	0.79	2.50	0.016
Mn	0.12	0.019	0.15	0.031	−3.83	0.000
Mg	20.9	0.89	21.0	0.98	−0.46	0.648
Ca*	−1.60	0.28	−0.85	0.73	−5.09	0.000
Cr*	3.77	0.08	3.66	0.12	3.87	0.000
V	79	7.1	70	7.9	4.55	0.000
Ni_{tot}*	3.38	0.11	3.35	0.06	−2.13	0.039
Ni_{sol}*	2.70	0.12	2.73	0.14	−1.13	0.264
Ni_{res}*	3.28	0.11	3.32	0.09	−1.69	0.096
Cu_{tot}*	1.85	0.37	1.52	0.56	2.53	0.015
Cu_{sol}*	1.38	0.46	1.27	0.63	0.70	0.487
Cu_{res}*	1.65	0.33	0.99	0.55	5.48	0.000

*: log-transformed variables.
The t-tests give a two-sample t-statistics in which the variance of each group is estimated separately. This was appropriate because F-tests showed that the variances in the two groups are different for most elements. The probability values listed corresponds to a two-sided test of significance when the samples are drawn from normal distributions. The probability values represent the probability of calculating a t statistic equal to, or more extreme than the t statistic listed, assuming the two groups to be derived from the same population.

criminant function correctly classifies 86% of the sterile samples and 100% of the fertile samples. Including additional variables does not significantly improve classification.

The discriminant function is given as:

$$F\ (ds) = 30.3\ Mn + 1.26\ Ca - 0.0677\ V - 3.20\ Cr - 0.387\ Fe + 17.8$$

The relative importance of the variables in the discriminant function is given by a discriminant function of standardized coefficients;

$$F\ (ds) = 0.78\ Mn + 0.71\ Ca - 0.51\ V - 0.32\ Cr - 0.32\ Fe$$

A histogram of discriminant scores is presented in Fig. 3. The quality of the function was checked with a bootstrap method (Diaconis and Efron, 1983). A random group consisting of 25% of the samples, was selected and these samples were classified using a discriminant function which was calculated with the remaining 75% of the samples. This procedure was repeated several times. The recalculated functions compared closely with the original and performed well
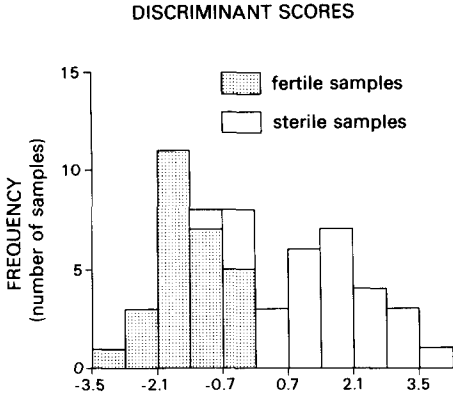
DISCRIMINANT SCORES

Fig. 3. Histogram of discriminant scores.

in classifying the test samples. Therefore, the function was found to be appropriate for use in the evaluation of the nickel-ore potential of serpentinite bodies in the Fortaleza de Minas greenstone belt.

NONLINEAR MAPPING AND FUZZY C-MEANS CLUSTERING

In the previous section it was shown with t-tests and discriminant analysis that fertile and sterile serpentinite samples can be discriminated using a relatively small number of chemical variables. However, discriminant function analysis does not provide insight into the multivariate data structure and gives no information on how well the pre-defined fertile and sterile groups actually form natural clusters in the multivariate data space. In this section we will use nonlinear mapping and fuzzy c-means clustering to examine if any natural clusters can be detected in the data or if the data form a more or less homogeneous group that is merely divided in the two parts by a discriminant analysis.

The nonlinear mapping algorithm was developed by Sammon (1969). The algorithm was applied to geochemical data by Garret (1973), Howarth (1973), Glasby et al. (1974), Howarth et al. (1977) and Chork and Govett (1985). Nonlinear mapping produces a two-dimensional projection of a multivariate data set so that the two-dimensional interpoint distances optimally approximate the original multivariate interpoint distances.

Fuzzy set theory was introduced by Zadeh (1965). Bezdek (1981) gave a review of fuzzy systems. Fuzzy cluster algorithms were applied to geochemical data by Granath (1984) and by Yu and Xie (1985). A combination of nonlinear mapping and fuzzy c-means clustering was used by Vriend et al. (1988) to find meaningful groupings in multivariate data sets.

Fuzzy c-means clustering is an iterative partitioning technique. These techniques are used if partitioning of the data in a pre-defined number of groups is appropriate (Howarth and Sinding-Larsen, 1983). In fuzzy c-means clustering

the fuzziness of the clustering is determined by the so-called q-parameter. The q-parameter can vary between 1 and infinity. For $q = 1$ fuzzy c-means clustering converges to hard c-means clustering. There is no theoretical basis for a choice of the q (Bezdek, 1981). A value of 1.5 was chosen which means that a fairly hard cluster solution is obtained.

Two functionals, the classification entropy and the partition coefficient give an indication of the significance of the obtained clusters. The functional values vary between 0 and 1. The entropy is closest to 0 and the partition coefficient is closest to 1 for the most significant clustering. The number of clusters for the serpentinite data was set to 2 in order to compare the correspondence of the fuzzy clusters with the pre-defined fertile and sterile groups. The two-cluster solution was also indicated by a minimum entropy and a maximum partition coefficient.

Variables used in the nonlinear mapping and fuzzy c-means clustering are Ti, Al, Fe, Mn, Ca, Cr, V, total Ni, residual Ni, total Cu and residual Cu. Si and Mg were not included in the analysis because of little variation of these variables over the total data and because part of the variation results from analytical precision which is of the same magnitude as the variation over the data. Soluble Ni and soluble Cu were not included because these variables showed a smaller contrast between the fertile and sterile groups than the total and residual Ni and Cu variables

Results of nonlinear mapping and fuzzy clustering are presented in Fig. 4. The nonlinear mapping shows that the fertile and sterile groups plot as a fairly homogeneous group. Most of the fertile samples plot in the upper part of the diagram and most of the sterile samples plot in the lower part. There is a good agreement between the sample configuration obtained by nonlinear mapping and fuzzy c-means clustering; samples with a high membership to cluster I plot in the upper part of the diagram and samples with a high membership to cluster II plot in the lower part. The two clusters obtained with fuzzy clustering correspond to the pre-defined fertile and sterile sample groups. However, a large portion of the samples shows an intermediate character indicated by shared membership of a sample to the clusters. A number of samples show a discrepancy between the obtained fuzzy clusters and nonlinear mapping configuration on the one hand and the pre-defined fertile and sterile association on the other hand. In discriminant analysis most of these samples show discriminant scores close to 0.

Nonlinear mapping and fuzzy c-means clustering indicate that the classification of the serpentinite samples into a fertile and sterile group is the most significant grouping in the data set. Although a discriminant analysis showed that the fertile and sterile groups can be clearly distinguished there is some overlap in chemical composition of fertile and sterile samples and the groups do not define well-separated clusters in multivariate data space.
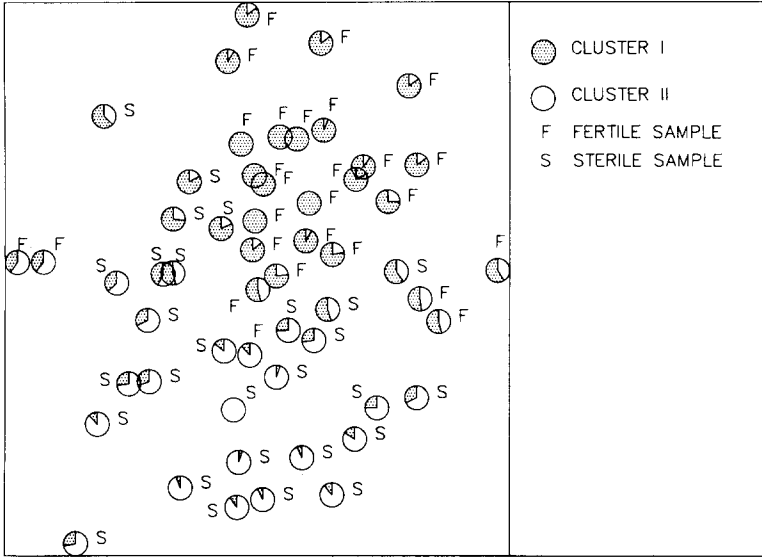
Fig. 4. Fuzzy c-means membership of serpentinite samples represented in a non-linear mapping plot.

DISCUSSION AND INTERPRETATION

The present study shows that fertile and sterile weathered serpentinites may be distinguished geochemically. Three processes are thought to be the most important in determining the chemical composition of the serpentinite surface rock: magmatic differentiation; sulphide saturation leading to chalcophile element depletion in ultramafic silicates within fertile serpentinites; and chemical weathering, considered to vary in intensity due to differences in the amount of sulphide and subsequent sulphuric acid generation in fertile and sterile serpentinites. Serpentinization can take place without significant metasomatism (Coleman and Keith, 1971; Komor et al., 1985; Donaldson et al., 1986) so that the serpentinization process is probably not as important as magmatic differentiation and sulphur saturation in generating Ni-sulphide ore bodies from ultramafic hosts or in generating the chemical signatures which distinguish the ultramafic hosts.

Factor analysis was thought to be useful to examine the relative importance of these processes and to indicate their respective contributions to the overall variability. However, it was found that significant differences in correlations between chemical variables in fertile and sterile serpentinites exist, which means that factor analysis should be applied on each group separately. Due to the fact that the two groups are rather small and therefore less suitable to be interpreted with a factor analysis (Howarth and Sinding-Larsen, 1983), a cor-

TABLE 3

Correlation matrix of chemical variables of fertile and sterile serpentinites

		Si	Mg	Fe	Al	Ti	Cr	Mn	V	Ni_{RES}	Ni_{SOL}	Cu_{RES}	Cu_{SOL}	Ca
Mg	F	0.56												
	S	0.55												
Fe	F		−0.27											
	S		0.44											
Al	F			−0.58										
	S			0.16										
Ti	F			−0.37	0.83									
	S			0.32	0.65									
Cr	F			−0.38	0.77	0.70								
	S			0.39	0.11	0.11								
Mn	F			0.44										
	S			0.29										
V	F	−0.03		0.28	0.35	0.50	0.46	0.20						
	S	0.38		0.63	0.40	0.49	0.36	0.37						
Ni_{RES}	F	0.38	0.31			0.20								
	S	0.20	0.53			−0.50								
Ni_{SOL}	F		0.24	0.38	−0.49		−0.53			0.78				
	S		−0.49	0.15	0.19		0.03			−0.25				
Cu_{RES}	F													
	S													
Cu_{SOL}	F			0.10					0.14		0.12	0.96		
	S			0.51					0.39		0.56	0.34		
Ca	F	−	−							−	−	−	−0.40	
	S	−0.38	−0.48							−0.40	0.59	−0.37		

F: fertile serpentinite.
S: sterile serpeninites.
Pairs of correlation coefficients listed are those with one value > 0.05 level of significance. (0.05 level of significance = 0.37.)
−: The correlation coefficient is not meaningful because the majority of the data are below the detection limit.

relation matrix of the chemical variables is presented in Table 3. Correlations between chemical variables of the fertile and sterile groups are listed. For a better understanding of the observed correlations a detailed mineralogical study is required, although some preliminary comments can be made.

Differences in primary mineralogy of the fertile and sterile serpentinites are thought to be indicated by the correlations between Ti, Al, Cr and V in the fertile serpentinites and the correlations of Ti, Al and V in sterile serpentinites. The correlations may be attributed to variations in ferrochromite spinel content and clinopyroxene content of the rocks. The larger part of these variations will arise from primary magmatic differences. Differences in degree of weathering, weathered rocks containing higher proportions of resistant and stable minerals like spinels, may also be important.

Sulphur saturation controls the overall ultramafic rock chemistry by bringing about the partitioning of chalcophile elements (Duke, 1979; Fleet and MacRae, 1983; Naldrett et al., 1984), enriching them in disseminated sulphides in the saturated magma and depleting them in the silicate minerals. This sulphide phase partitioning is believed to account for Cu enrichment and residual Ni depletion in weathered fertile serpentinites. In contrast to the behaviour of Ni in the fertile serpentinite, the positive correlation of Mg and residual Ni in sterile serpentinites may indicate that the residual Ni content is related to the primary olivine content of these rocks. Additionally, in weathered sterile serpentinites Ni and Cu, released in the weathering of silicates and sulphides, remain in situ and higher portions of total Ni and total Cu are present in their ascorbic acid-hydrogen peroxide-soluble form.

Disseminated sulphide affects weathered ultramafic rock chemistry by controlling the pH of weathering via sulphide oxidation and subsequent sulphuric acid generation. The pH is considered to be the controlling factor in the decomposition of serpentine (Nickel et al., 1977). Unweathered fertile serpentinites in the Fortaleza de Minas greenstone belt have a measured sulphide content on the order of 0.2% as compared with only 0.04% sulphide in unweathered sterile serpentinites. Higher sulphide concentrations in fertile serpentinites cause stronger chemical weathering due to decomposition of sulphides and hydrolysis of Fe^{3+} (Nickel and Thornber, 1977). The very low Ca content and lower soluble Ni content of the fertile serpentinite indicate the influence of sulphide in leaching of the serpentinites during tropical weathering. In the absence of strong acid solutions, weathering proceeds in the sterile serpentinites without strong leaching of Ca, soluble Ni and soluble Cu. Ca is present in both fertile and sterile fresh serpentinites as carbonates and tremolite. In weathered serpentinites carbonates were found to be absent in samples with a Ca content below detection limit (Gaspar, 1985) and thus it is likely that Ca in these rocks is expressed mainly as carbonate.

Individual element enrichment and depletion determined from t-tests and correlation coefficients between chemical variables can be explained in terms

of magmatic differentiation, sulphide saturation and chemical weathering of the serpentinite surface rocks. More detailed mineralogical information is necessary to evaluate the contribution of each process in determining the serpentinite surface rock composition.

CONCLUSIONS

In the tropical weathering environment of southwestern Minas Gerais, Brazil, it is possible to discriminate fertile, Ni-sulphide-bearing, serpentinites from sterile, Ni-sulphide-free, serpentinites using total-metal analyses of Cu, Ni and Al, Ca, Cr, Fe, Mg, Mn, Si, Ti, and V along with ascorbic acid, hydrogen peroxide extractible analyses of Ni and Cu. Results from the analyses indicate that the weathered fertile serpentinites are enriched in total Cu, residual Cu, total Ni, Al, Cr, Ti, Fe and V and depleted in residual Ni, Ca and Mn with respect to their weathered sterile counterparts. Student's t-tests, discriminant analyses, nonlinear mapping and fuzzy c-means clustering help to better define existing metal differences between fertile and sterile serpentinites and to statistically distinguish the two serpentinite rock types.

Lithogeochemical evaluation of weathered serpentinites is considered to be a useful cost-effective approach in explorating for ultramafic-hosted Ni-sulphide mineralization. It can serve as a complement to gossan search and as an approach towards finding blind mineralization when weathered sulphide or gossan is unexposed, but where the potential Ni-sulphide-bearing ultramafic host rock is available for surface rock sampling.

ACKNOWLEDGEMENTS

REFERENCES

Bezdek, C.J., 1981. Pattern Recognition with fuzzy objective function algorithms. Plenum Press, New York, NY, 225 pp.

Buchanan, D.L. and Nolan, J., 1979. Solubility of sulfur and sulfide immiscibility in synthetic tholeiitic melts and their relevance to Bushveld-complex rocks. Can. Mineral., 17: 483–494.

Bull, A.J. and Mazzucchelli, R.H., 1975. Application of discriminant analysis to the geochemical evaluation of gossans. In: I.L. Elliott and W.K. Fletcher (Editors), Geochemical Exploration 1974. Elsevier, Amsterdam, pp. 219-226.

Cameron, E.M., Siddely, G. and Durham, C.C., 1971. Distribution of ore elements in rocks for evaluating ore potential: nickel, copper, cobalt and sulphur in ultrmafic rocks of the Canadian shield. C.I.M. Spec. Vol., 11: 298-313.

Campbell, I.H., Naldrett, A.J. and Roeder, P.L., 1979. Nickel activity in silicate liquids: some preliminary results. Can. Mineral., 17: 495-505.

Chork, C.Y. and Govett, G.J.S., 1985. Comparison of interpretations of geochemical soil data by some multivariate statistical methods, Key Anacon, N.B., Canada. J. Geochem. Explor., 23: 213-242.

Coleman, R.G. and Keith, T.E., 1971. A chemical study of serpentinization at Burro Mountain, California. J. Petrol., 12(2): 311-328.

Diaconis, P. and Efron, B., 1983. Computer-intensive methods in statistics. Sci. Am., 248: 96-108.

Donaldson, M.J., Lesher, C.M., Groves, D.I. and Gresham, J.J., 1986. Comparison of Archean dunites and komatiites associated with nickel mineralisation in Western Australia: Implications for dunite genesis. Miner. Deposita, 21: 296-305.

Duke, J.M., 1979. Computer simulation of the fractionation of olivine and sulfide from mafic and ultramafic magmas. Can. Mineral., 17: 507-514.

Fleet, M.E. and MacRae, N.D., 1983. Partitioning of Ni between olivine and sulfide and its application to Ni-Cu sulfide deposits. Contrib. Mineral. Petrol., 83: 75-81.

Galvão, M.V. (Editor), 1977. Geografia do Brasil, Regiao Sudeste, Vol. 3. Fundação Instituto Brasileiro de Geografia e Estatìstica (I.B.G.E.), Rio de Janeiro, 667 pp.

Garrett, R.G., 1973. Regional geochemical study of Cretaceous acidic rocks in the northern Canadian Cordillera as a tool for broad mineral exploration. In: M.J. Jones (Editor), Geochemical Exploration 1972. Institution of Mining and Metallurgy, London, pp. 259-273.

Gaspar, J.C., 1985. Estudo Comparativo entre ò serpentinito mineralizado O'Toole e serpentinitos estereis. B.P. Mineração LTDA., intern. mem.

Glasby, G.P., Tooms, J.S. and Howarth, R.J., 1974. Geochemistry of manganese concretions from the northwest Indian Ocean. N. Z. J. Sci. 17: 387-407.

Govett, G.J.S., 1972. Interpretation of a rock geochemical exploration survey in Cyprus — statistical and graphical techniques. J. Geochem. Explor., 1: 77-102.

Granath, G., 1984. Application of fuzzy clustering and fuzzy classification to evaluate the provenance of glacial till. Math. Geol., 16, 283-301.

Groves, D.I., Barrett, F.M. and McQueen, K.G., 1979. The relative roles of magmatic segregation, volcanic exhalation and regional metamorphism in the generation of volcanic-associated nickel ores of Western Australia. Can. Mineral., 17: 319-336.

Häkli, A., 1963. Distribution of nickel between the silicate and sulphide phases in some basic intrusions in Finland. PhD. Thesis, Bull. Com. Geol. Finlande, 209.

Howarth, R.J., 1973. Preliminary assessment of a non-linear mapping algorithm in a geological context. Math. Geol., 5: 39-57.

Howarth, R.J. and Sinding-Larsen, R., 1983. Multivariate analysis. In: G.J.S. Govett and R.J. Howarth (Editors), Handbook of Exploration Geochemistry, Vol. 2: Statistics and Data Analysis in Geochemical Prospecting. Elsevier, Amsterdam, pp. 207-283

Howarth, R.J., Cronan, D.S. and Glasby, G.P., 1977. Non-linear mapping of regional geochemical variability of manganese nodules in the Pacific Ocean. Trans. Inst. Min. Metall. London 86, B4-B16.

Komor, S.C., Elthon, D. and Casey, J.F., 1985. Serpentinization of cumulate ultramafic rocks from the North Arm Mountain Massif of the Bay of Islands ophiolite. Geochim. Cosmochim. Acta, 49: 2331-2338.

Lynch, J.J., 1971. The determination of copper, nickel and cobalt in rocks by atomic absorption spectrometry using a cold leach. C.I.M. Spec. Vol., 11: 313–314.

Moeskops, P.G., 1977. Yilgarn nickel gossan geochemistry: a review with new data. J. Geochem. Explor., 8: 247–258.

Naldrett, A.J., Duke, J.M., Lightfoot, P.C., Thompson, J.F.H., 1984. Quantitative modelling of the segregation of magmatic sulphides: an exploration guide. C.I.M. Bull., 77 (864): 46–56.

Nickel, E.H. and Thornber, M.R., 1977. Chemical constraints on the weathering of serpentinites containing nickel-iron sulphides. In: C.R.M. Butt and I.G.P. Wilding (Editors), Geochemical Exploration 1976. Elsevier, Amsterdam, pp. 235–245.

Nickel, E.H., Allchurch, P.D., Mason, M.G. and Wilmshust, J.R., 1977. Supergene alteration at the Perseverance nickel deposit, Agnew, Western Australia. Econ. Geol., 69: 93–107.

Sammon, J.W., 1969. A non-linear mapping for data structure analysis. IEEE Trans. Comput. C18, 401–409.

Spray, J.G., 1985. Some preliminary observations on the stratigraphy, structure and southeast margin fault control of the O'Toole nickel orebody, Fortaleza de Minas, Brazil. Dept. of Earth Sci., Univ. of Cambridge, Cambridge, U.K.

Teixeira, N.A. and Danni, J.C.M., 1979. Geologia da raíz de um greenstone belt na região de Fortaleza de Minas, Minas Gerais. Rev. Bras Geoc. (São Paulo), 9 (1): 17–26.

Vriend, S.P., van Gaans, P.F.M., Middelburg, J. and de Nijs, A., 1988. The application of fuzzy c-means cluster analysis and non-linear mapping to geochemical datasets: examples from Portugal. Appl. Geochem., 3: 213–224.

Wilmshurst, J.R., 1975. The weathering products of nickeliferous sulphides and their associated rocks in Western Australia. In: I.L. Elliott and W.K. Fletcher (Editors), Geochemical Exploration 1974. Elsevier, Amsterdam, pp. 417–436.

Yu Bochang and Xie Xuejing, 1985. Fuzzy cluster analysis in geochemical exploration. J. Geochem. Explor., 23, 281–291.

Zadeh, L.A., 1965. Fuzzy sets. Inf. Control, 8: 338–353.