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Attempts at a Quantitative Laser Microprobe Analysis of Rocks*

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(With 5 Tables and 4 Figures)

A laser microprobe analyser was recently employed for the quantitative analysis of some materials such as alloys (cf. KUBOTA, 1971). The quantitative analysis of silicate using this instrument is not yet in common currency; the work of BLACKBURN *et al.* (1968) on garnet is the only example the authors are aware. The impossibility of adding an internal standard is the principal problem with this technique.

The present authors wish to analyse rocks and minerals quantitatively by this method, the qualitative analysis having already been tried by the same authors (YOSHIDA *et al.*, 1974). In the experiments described in the present article, the authors tried to obtain calibration curves of some elements of rocks using standard rock samples (geochemical standards of JG-1 and JB-1, prepared by the Geological Survey of Japan).

The results were somewhat valuable. Good calibration curves of some elements were able to be drawn. Thus it is not unreasonable to estimate the comparative amount of some elements in qualitative analysis using a laser microprobe as was done by YOSHIDA *et al.* (1974). The quantitative analysis of rocks using this method has also come to be considered possible.

Apparatus and operating conditions

Laser microprobe: JEOL JLM-200, with Nd^{3+} glass laser, laser output of 1.5 joules, laser wavelength of 1.06 μm, with a 7 mm aperture (beam screen), auxiliary spark with graphite of 3 mm in diameter, 2.4 kV, 150 μmH, 11 μmF, 1 Ω, electrode gap of 1.3 mm, set 1 mm above the surface of the sample, Olympus MF type microscope with M5× objective lens, single shot method.
Spectrograph: JEOL JLM-125 type (plane grating spectrograph), with grating of 1200 grooves/mm, 0.05 Å in resolving power, F/10.9 aperture ratio, reciprocal linear dispersion value (first order) of 6.2 Å/mm, slit width of 10 μm, Kodak SA-3 type photoplate, development time, using D-19, 5 minutes (at 20°C), with the wavelength range set at 2183–3683 Å.
Microphotometer: JEOL JLM-1A type, slit width 20 μm, slit height 600 μm, scan selection 1.0 cm/min, with dials set at Sensitivity 4, Brightness 3.7, and Density 1 or 2. Full count (100) was determined by setting the density of the spectral line of Si at about 70. Zero calibration was made in the base of the photoplate.
Microphotometer recorder: Hokushin laboratory recorder, Hokushin T-D interface type, with a range of 10 mV and a chart speed of 40 mm/min.

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Sample preparation

The analytical standard series was prepared by mixing geochemical standards of JG-1 granodiorite and JB-1 basalt prepared by the Geological Survey of Japan (ANDO *et al.*, 1974), then by adding lithium tetraborate (anhydrous), as prepared by the Research Co., and finally by melting this material into glass, using a Philips semiautomatic borax bead preparation machine. Thus standard glass samples of the GB standard series (GB1–GB5), composed of mixtures of JB-1 and JG-1 in ratios of 1:0, 3:1, 1:1, 1:3, and 0:1, to which an equal amount of lithium tetraborate was added, and those of the B standard series (B2, B1, B4, and B5), composed of mixtures of JB-1 and lithium tetraborate in ratios of 1:3, 1:1, 5:3, and 3:1, were obtained (Tables 1 and 2).

Table 1. GB standard series (weight ratio of analysed elements to Si expressed as a percentage)

	GB-1	GB-2	GB-3	GB-4	GB-5
	x/Si %	*x*/Si %	*x*/Si %	*x*/Si %	*x*/Si %
Fe	26	20.6	15.2	9.88	4.5
Mg	19	14.6	10.2	5.7	1.3
Cr	0.093	0.0717	0.0503	0.0290	0.0076
V	0.066	0.0504	0.0348	0.0192	0.0036
Ca	27	21.4	15.9	10.3	4.7
Cu	0.012	0.00928	0.00655	0.00383	0.0011
Ti	3.3	2.59	1.87	1.16	0.44
Ni	0.031	0.0236	0.0162	0.00880	0.0014

Table 2. B standard series (content of JB-1 in B standard series, which is composed of JB-1 + lithium tetraborate)

	JB-1 / JB-1 + lithium tetraborate
B-2	0.25
B-1	0.5
B-4	0.625
B-5	0.75

The standard glass samples thus made were disc-formed, being about 3 cm in diameter and 3 mm in thickness, with flat planes on the top and bottom sides. Standard glass samples are faintly smoky and pale to deep gray with a brownish tint. The clearness and color of all these standard glass samples are practically homogeneous.

Analytical procedure

Three scattered points on the bottom palne of each of the standard glass samples were shot with a laser, and accordingly three spectra were recorded on a photoplate. Thus 15 spectra of the GB standard series and 12 spectra of the B standard series were recorded,

Table 3. Spectral lines of the analysed elements (Å)

Si	2987.648
Fe	2382.039
Mg	2779.834
Cr	2835.633
V	3110.706
Ca	3158.869
Cu	3247.540
Ti	3372.800
Ni	3414.765

Table 4. Density ratios of spectral lines of analysed elements to that of Si, in GB standard series

	Photoplate No. -Spectrum No.	Fe	Mg	Cr	V	Ca	Cu	Ti	Ni
GB-1	750401–1	1.20	1.34	0.658	0.319	1.67	0.681	1.61	0.370
	750401–2	1.30	1.44	0.648	0.252	1.81	0.625	1.77	0.271
	750401–3	1.24	1.40	0.609	0.255	1.80	0.721	1.75	0.302
	Average	1.25	1.39	0.638	0.275	1.76	0.676	1.71	0.341
GB-2	750402–13	1.24	1.38	0.454	0.138	1.58	0.431	1.48	0.241
	750402–14	1.08	1.34	0.518	0.198	1.51	0.748	1.47	0.242
	750402–15	1.08	1.34	0.505	0.247	1.50	0.525	1.44	0.231
	Average	1.13	1.35	0.492	0.194	1.53	0.568	1.46	0.238
GB-3	750401–4	1.18	1.22	0.479	0.161	1.62	0.292	1.52	0.155
	750401–5	1.28	1.30	0.494	0.140	1.71	0.252	1.58	0.0981
	750401–6	1.17	1.17	0.463	0.121	1.58	0.567	1.47	0.161
	Average	1.21	1.23	0.479	0.141	1.64	0.373	1.52	0.138
GB-4	750402–16	1.06	0.965	0.282	nd	1.26	0.225	1.18	0.101
	750402–17	1.13	1.08	0.394	nd	1.39	0.193	1.21	0.0911
	750402–18	1.35	1.07	0.512	nd	1.54	0.188	1.35	0.0766
	Average	1.18	1.04	0.396	—	1.40	0.202	1.25	0.0896
GB-5	750401–7	1.06	0.329	0.301	nd	0.845	0.167	0.793	nd
	750401–8	1.03	0.263	0.295	nd	0.880	0.137	0.764	nd
	750401–9	0.849	0.354	0.278	nd	0.839	0.147	0.741	nd
	Average	0.980	0.315	0.291	—	0.855	0.150	0.766	—

among which, GB1, 3, and 5 were recorded on photoplate No. 750401 and others on photoplate No. 750402.

Eight elements, amounts of which vary considerably compared with other elements in GB standard series from GB1 to GB5, were selected for analysis. To each of these elements, a spectral line, the density of which was most convenient for microphotometer

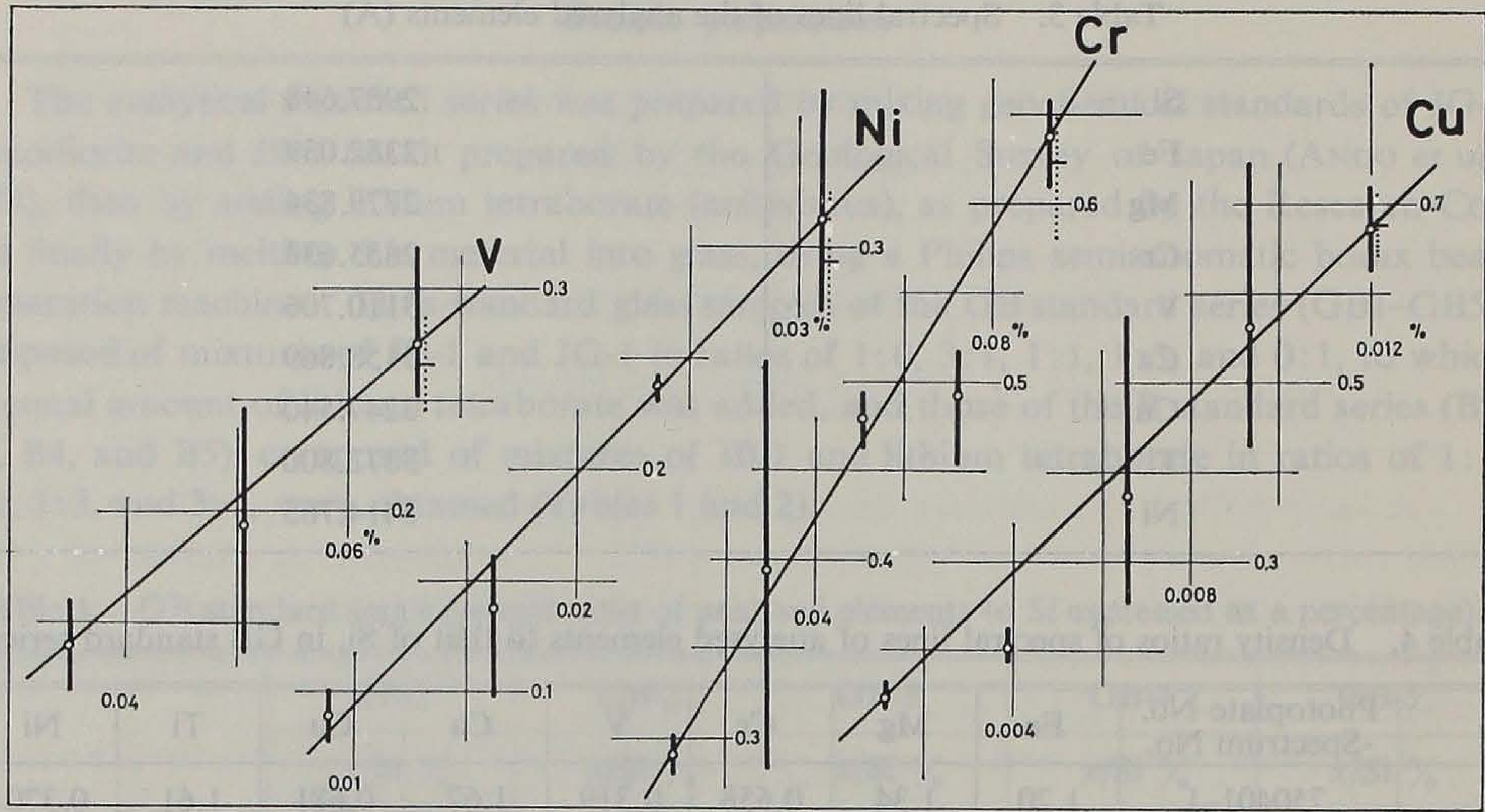

Fig. 1. Relation between density ratio and weight ratio of the minor elements to Si, in the GB standard series

The thick solid line indicates the range of ratios of three analyses. The small open circle shows an average ratio of the three analyses. The dotted line with the bar is the range (and the bar is an average) of three analyses of the B1 standard glass sample.

measurement, was chosen (Table 3). The density of each spectral line was recorded in chart form and measured by subtracting the background value (measured by continuing the lowest values which are found within several centimeters, *vis.* some Å, from both sides of the object peak) from the peak value.

Results

Densities of the spectral lines of the selected elements of the GB standard series were compared with that of Si (Table 4). In Figs. 1 and 2, this density ratio of an element to Si is plotted against the weight ratio of the element to Si. The plots of each element give straight or curve lines with a positive inclination. Lines of Cr, V, Cu, and Ni, which are minor components, are straight, while those of Fe, Mg, Ca, and Ti, which are major components, are convex. In the graph, plots of each analysis of some of these elements scatter considerably, the scattering of Fe being the greatest. But plots of an average value of three analyses of any one element do not scatter significantly*. Thus most of these lines, except the upper part of the lines of the major elements, are able to be used as calibration curves; quantitative laser microprobe analysis of some components of rocks may be

* GB2 and 4 were analysed on a different day, after GB1, 3, and 5 were analysed; hence GB2 and 4 were recorded on a different photoplate from that of GB1, 3, and 5. This may partly explain the sporadic deviations of plots of GB2 in Figs. 1 and 2.

On the other hand, plots of B1 (this has the same composition as GB1 but was prepared separately as a different glass sample from that of GB1), GB4, and most of GB2 coincide well on calibration curves or participate well in drawing smooth calibration curves. This may be a good support of the validity of the calibration curves.

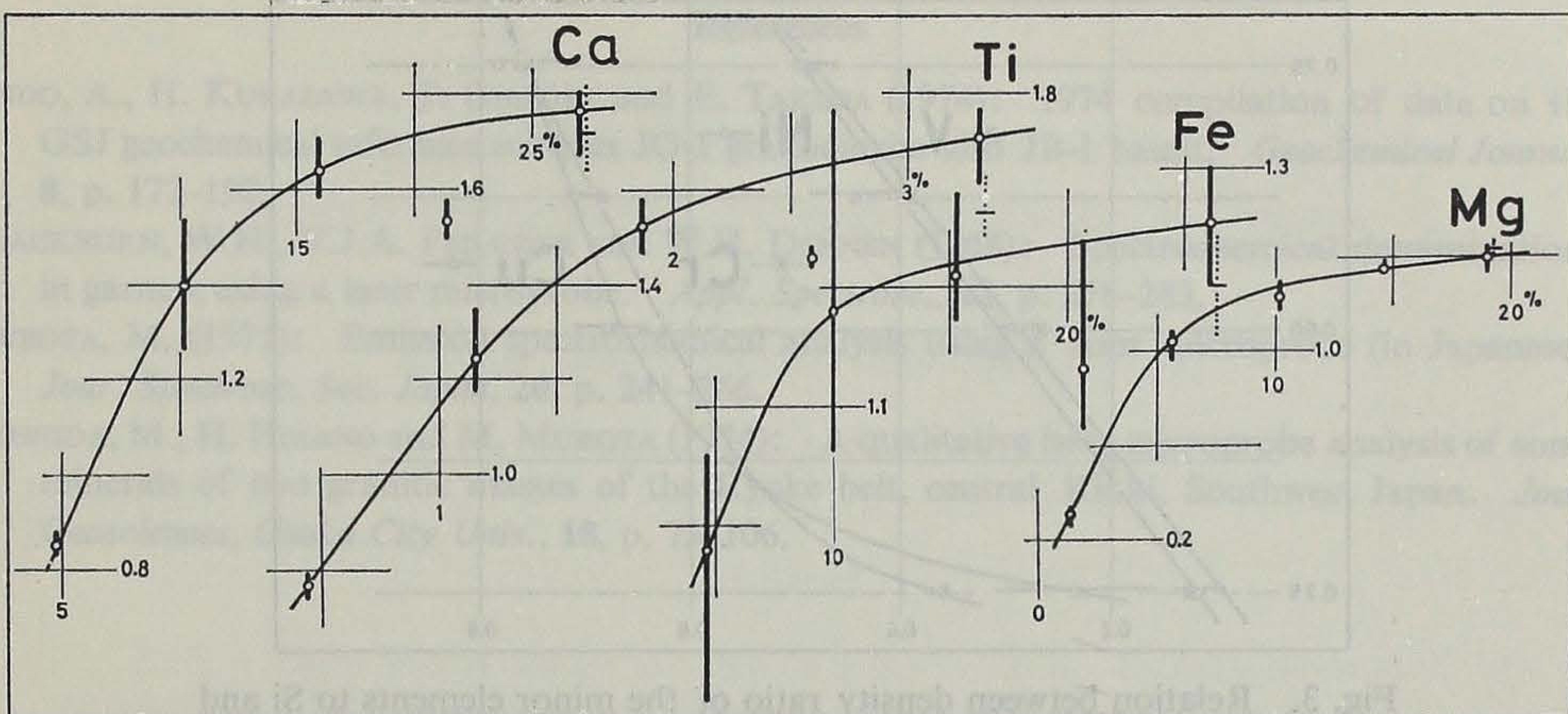

Fig. 2. Relation between density ratio and weight ratio of the major elements to Si, in the GB standard series
Symbols are the same as in Figure 1.

possible, fusing the rocks with lithium tetraborate and using such calibration curves as presented above.

The results of the analyses of the B standard series are given in Table 5 and Figs. 3 and 4. The density ratio of the spectral line of any one element to that of Si changes

Table 5. Density ratios of spectral lines of analysed elements to that of Si, in B standard series (No. 2 was low in radiation and therefore it was impossible to obtain any ratios)

	Photoplate No. -Spectrum No.	Fe	Mg	Cr	V	Ca	Cu	Ti	Ni
B-2	750402–1	0.826	0.886	0.335	0.0976	1.14	0.310	1.04	0.096
	750402–2	nd	nd	nd	nd	nd	nd	nd	nd
	750402–3	0.808	1.06	0.376	0.172	1.53	0.155	1.15	0.138
	Average	0.817	0.973	0.356	0.126	1.34	0.233	1.10	0.117
B-1	750402–4	1.21	1.42	0.581	0.247	1.64	0.711	1.50	0.289
	750402–5	1.16	1.43	0.641	0.288	1.71	0.680	1.53	0.323
	750402–6	1.24	1.46	0.647	0.267	1.82	0.646	1.62	0.267
	Average	1.20	1.44	0.623	0.267	1.72	0.679	1.55	0.293
B-4	750402–7	0.986	1.29	0.599	0.323	1.55	0.696	1.43	0.381
	750402–8	0.938	1.19	0.730	0.438	1.40	0.714	1.30	0.487
	750402–9	0.952	1.19	0.710	0.404	1.47	0.716	1.37	0.460
	Average	0.959	1.22	0.680	0.388	1.47	0.709	1.37	0.443
B-5	750402–10	0.822	1.16	0.757	0.505	1.40	0.761	1.28	0.508
	750402–11	0.935	1.22	0.740	0.453	1.48	0.795	1.39	0.503
	750402–12	0.909	1.20	0.766	0.496	1.44	0.724	1.33	0.462
	Average	0.889	1.19	0.754	0.485	1.44	0.760	1.33	0.491

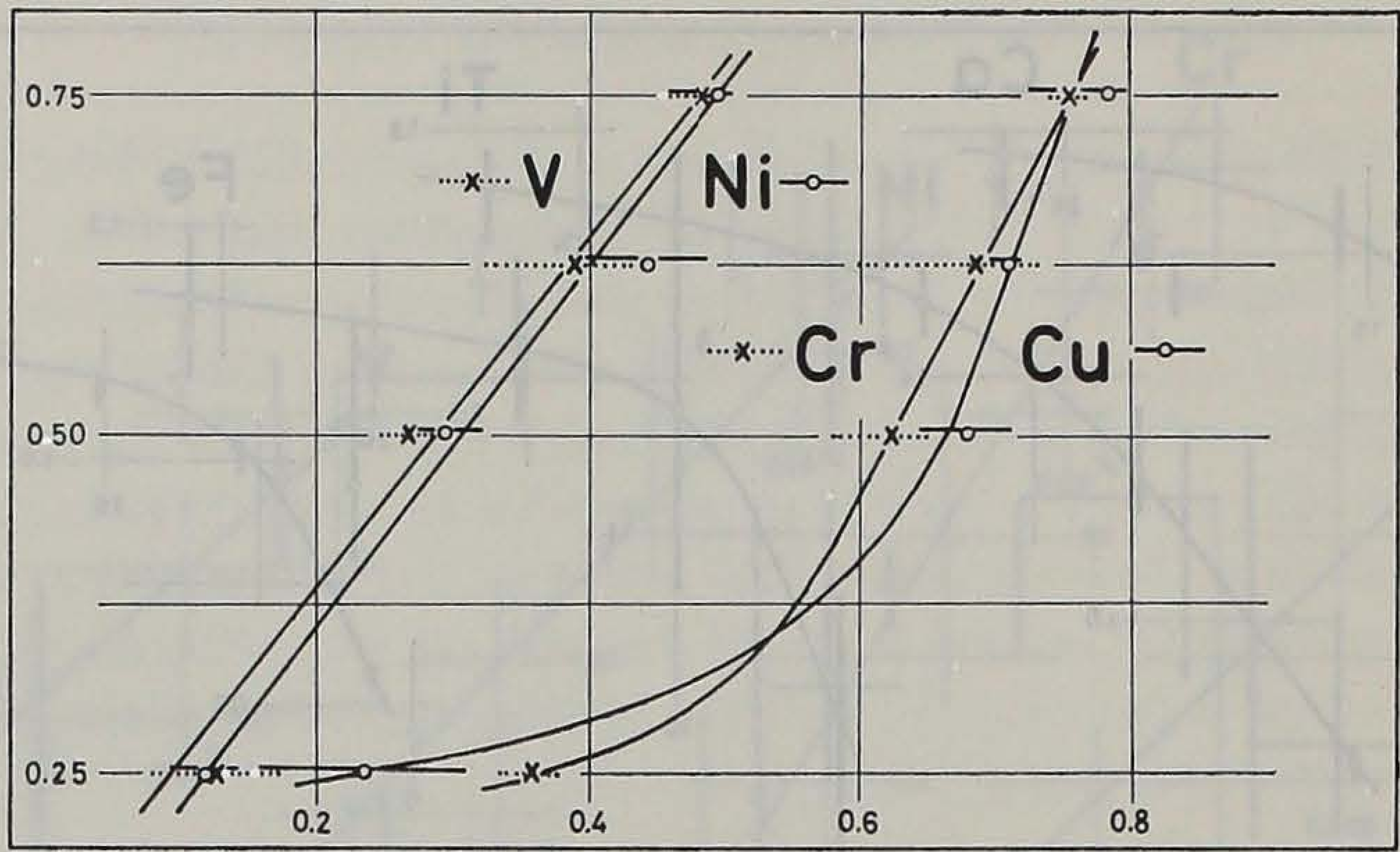

Fig. 3. Relation between density ratio of the minor elements to Si and weight ratio of JB-1, in the B standard series
Solid or dotted lines with small open circles or crosses indicate the range of ratios and an average of the three analyses.

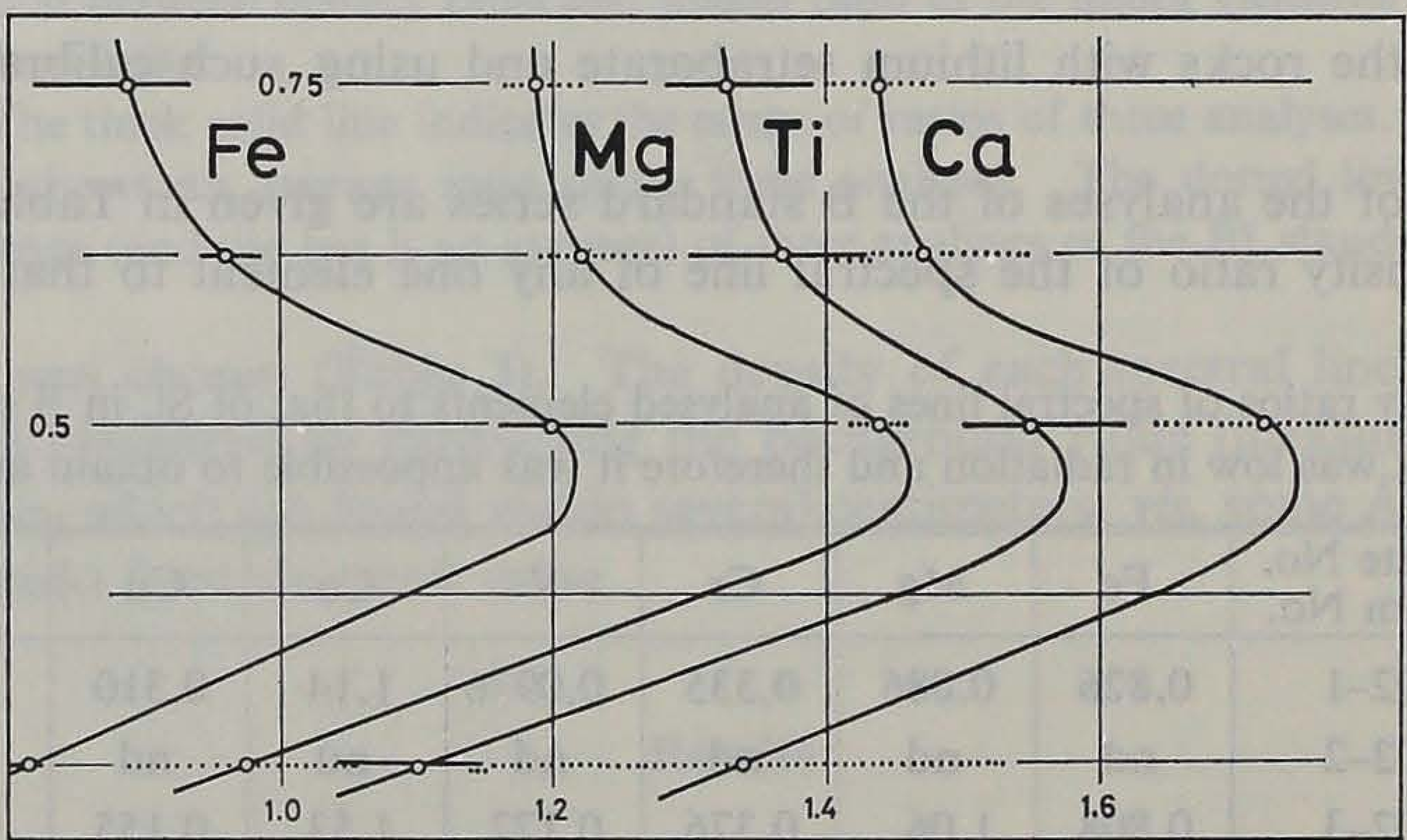

Fig. 4. Relation between density ratio of the major elements to Si and weight ratio of JB-1, in the B standard series
Symbols are the same as in Figure 3.

regularly, corresponding to the change in the weight percent of JB-1 in the glass samples. Thus the calibration curves of Figs. 1 and 2 can be corrected into new calibration curves for some elements in silicate materials without lithium tetraborate; quantitative laser microprobe analysis of minerals in a thin section of rocks has come to be considered possible.

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