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An evaluation of the performance of an inductively coupled plasma source spectrometer for the determination of the major and trace constituents of silicate rocks and minerals

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SUMMARY. The results of a study on the suitability of the inductively coupled plasma source spectrometer for the analysis of rocks and minerals are presented. The preparation of a stable solution of the elements to be measured is a prerequisite, and methods of sample preparation are described. It is shown that it is possible to measure all the major elements (excluding H_2O and Fe^{2+}) with acceptable precision and accuracy, and a wide range of trace elements down to the ppm level in the rock or mineral. Excluding sample preparation time, analysis and print-out of results as percent or ppm requires 1-2 minutes for complete analysis. Data on possible interferences (spectral line overlap etc.) are presented and, using some analyses of rocks and minerals comparisons are made with other analytical methods.

THE analysis of silicate materials presents one of the most severe tests of any analytical method, not only because of the range of compositions found but also because of the refractory nature of many of the minerals present. The analyst's problems are compounded by the increasing numbers of analyses required for modern geochemical work and the greater number of elements requiring determination. In consequence the traditional 'classical' methods (Washington, 1930) have been largely replaced by more rapid instrumental methods. These instrumental methods have included colorimetric procedures (Riley, 1958; Sandell, 1959), atomic absorption (Angino and Billings, 1972), and particularly X-ray fluorescence procedures (Leake *et al.*, 1969). Activation analysis and isotope dilution have also been used for the determination of selected elements. All these methods have considerable advantages but all have limitations, and the need to investigate alternative methods of silicate analysis has not decreased with the refinements in these methods.

One alternative analytical method that would appear to be especially suited to silicate analysis is inductively coupled plasma (ICP) emission spectrometry. In theory it should be possible to measure the great majority of elements in the periodic table, with low detection limits, good precisions, and linear calibrations over several orders of magnitude, enabling major and trace elements to be determined. As it is a solution method, matrix effects can be minimized and chemical interference effects appear to be negligible. Most important, all the elements can be measured simultaneously in a matter of seconds, making it apparently the most rapid of all analytical methods. The cost of the capital equipment is below that of a comparable sequential XRF system and the cost per analysis should be very competitive.

The purpose of this paper is to present the results of a detailed investigation into the advantages, and limitations, of the inductively coupled plasma source spectrometer for the analysis of the major and trace constituents of silicate rocks. The results and procedures documented here should be applicable to other ICP systems for silicates, and indeed assist in the analysis of other inorganic materials.

General

The basic research work on the incorporation of inductively coupled plasmas into an analytical system has been documented elsewhere, and several manufacturers can now offer analytical systems; summaries of the method include Fassel and Kniseley (1974), Greenfield *et al.* (1975), Boumans and de Boer (1975), Boumans (1978), and Fassel (1978).

In present usage the method is a solution method and it is a prerequisite that elements which are to be analysed are present in aqueous solution (see solution procedures below). The solution is pumped by a peristaltic pump into a spray chamber where the flow of pure argon gas converts a proportion of the solution to an aerosol and this is then sprayed into the centre of an argon plasma. The inductively coupled plasma is a stream of argon atoms which are heated by inductive heating using a radio frequency coil which is run from a Colpitts type C generator. Inductive heating of the argon as it flows through the r.f. field effectively strips electrons away from the argon atoms and produces a plasma of argon ions with an operating temperature in its centre of 6000–10000 °K; the plasma is ignited by a high-frequency Tesla spark. In the equipment used in this work (the Philips/MBLE system) the r.f. generator is free running and operates at a nominal 50 MHz. The glass torch in which the plasma is generated is cooled by the outer part of the flow of argon gas. The analytical system is shown schematically in fig. 1.

The solution to be analysed is thus sprayed into a very-high-temperature flame; this flame is stable and of sufficient temperature to dissociate the chemical bonds and excite a very large number of intense spectral lines. The light emitted is then focused into a conventional air path 1.5 m spectrometer (fig. 1), in which the spectral lines diffracted from the main grating are detected by fixed photomultipliers mounted along the Rowland circle of the spectrometer. The signal from the photomultipliers may be output directly on to the teletype to give intensity measurements. Alternatively, calibration lines can be prepared from the intensity readings obtained from solutions containing known concentrations of the elements, and these calibration lines may be stored in the computer linked to the system.

The data-processing analytical package supplied by Philips with the P852 computer (CESPEC III) was used for all the work done in this study with the calibrated lines, and it is possible after calibration of the instrument to output (on a teletype)

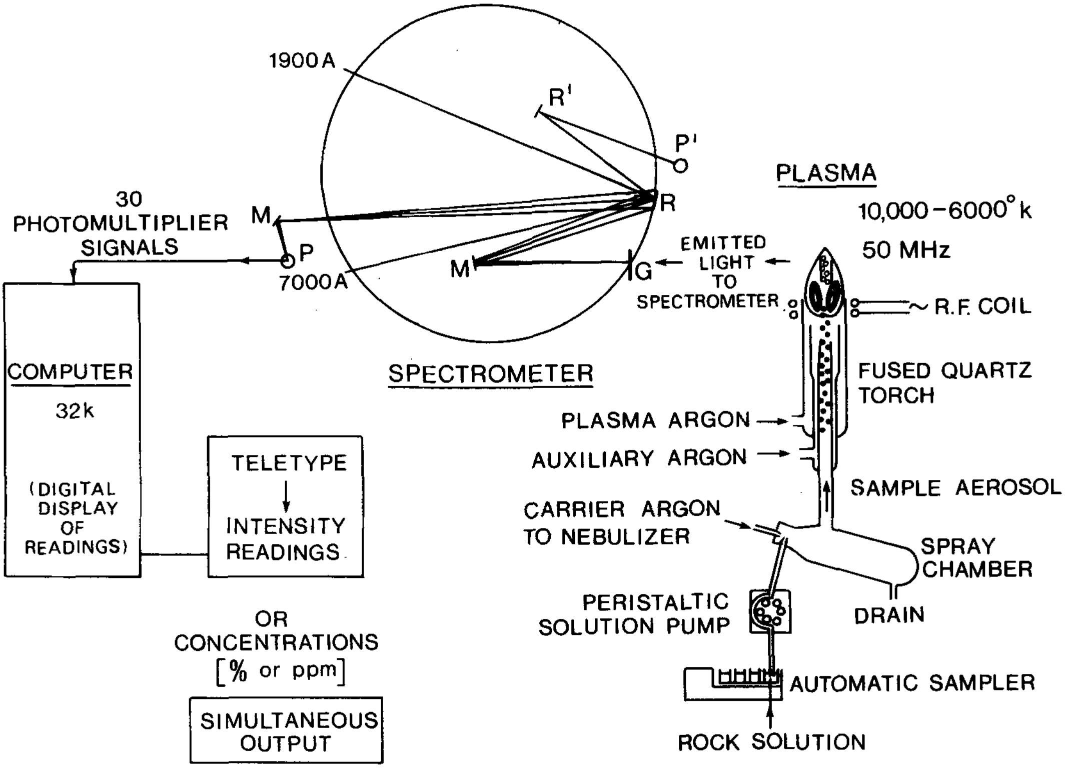

Fig. 1. ICP source spectrometer layout. Rock solution is pumped into a spray chamber where a proportion of the solution is converted to an aerosol by the cross-flow of argon gas. This aerosol then enters the centre of the plasma flame, and the light emitted enters the spectrometer through a 20 μm slit (G); this is reflected from mirror (M) and diffracted from the main spectrometer grating (R). The spectral lines are reflected on to their respective photomultipliers (only one is shown in the diagram). One photomultiplier may be moved through the spectral range (1900–7000 Å, or 190.0–700.0 nm). The *K* line lies outside this range (766.49 nm) and to measure this line the zero-order light is diffracted from a second grating (R′) on to another photomultiplier (P′).

analyses directly as concentrations in per cent or ppm, each complete analysis requiring only 1-2 min, excluding sample preparation time.

Solution preparation techniques

It is necessary to prepare stable solutions for all the elements to be determined in ICP spectrometry, and it was found advantageous to prepare two solutions, one that is used primarily for major-element work by fusion with lithium metaborate (following Suhr and Ingamells, 1966, and Ingamells, 1966), and the other used primarily for trace-element work from an $HF/HClO_4$ attack.

Major elements procedure. The rock powder (0.5 g) is weighed accurately into a platinum crucible and 1.5 g of $LiBO_2$ added. These are carefully mixed with a thin platinum rod and fused over a Meker burner for 30 min, occasionally swirling the fused mixture gently. The crucible is allowed to cool to room temperature and immersed in a polythene beaker which contains 165 ml (approximately) distilled water and 10 ml conc. HNO_3; 20 ml (precisely) of 1250 μg/ml $La(NO_3)_3$ solution is added as an internal standard. A p.t.f.e.-coated magnetic stirring bead is placed inside the crucible (which must be entirely immersed in the solution) and stirred *immediately*. The solution is diluted to 250 ml after complete dissolution of the fusion bead (1-2 hr). It is important to follow the procedure closely to prevent the formation of insoluble polysilicic acid, but if properly prepared the solutions have been found to be stable over a period of several months using a wide range of rock and mineral compositions.

Trace-elements procedure. The powdered rock (0.5 g) is evaporated almost to dryness with 4 ml of $HClO_4$ and 15 ml of HF, and dissolved in 4 ml of $HClO_4$ and 15 ml of distilled water before diluting to 50 ml. This is a well-established procedure and follows Riley (1958). Si is removed in the evaporation, but all the other major elements and the trace elements can be determined on this more concentrated solution. The solution must be carefully inspected for any residual refractory minerals.

Instrumental parameters

Instrument settings have been studied in some detail with a view to obtaining the best compromise conditions for all the elements it was hoped to measure. It was decided that it would be undesirable to optimize instrument settings for one element if this resulted in a serious deterioration in performance for other important elements. Perhaps the greatest single advantage of ICP analysis is the ability to measure many elements simultaneously and this advantage should not be lost if at all possible. Thus the instrument settings given in Table I are not necessarily the best for each individual element. For example, changing observation height above the plasma produced significant variations in the intensity output for the different elements. However, in practice it proved relatively easy to establish compromise conditions, most elements giving acceptable results over a range of instrument settings.

TABLE I. *Instrument settings used for ICP analysis of silicates.* (a) *for major elements with $LiBO_2$ fusion solutions;* (b) *for trace elements using $HF/HClO_4$ evaporations*

	(a)	*(b)*
RF generator	1.4 kW	1.2 kW
Gas flows (all high-purity argon):	litres/min	
Plasma (and coolant)	20	18
Auxiliary	0.5	0
Carrier	1.3	1.3
Sample uptake rate	2.3	

The most critical parameter so far as both detection limits and precision are concerned was the carrier gas flow, and careful control and stabilization of this gas flow proved to be absolutely essential to achieve good results with the ICP spectrometer system. Previous work on the optimization of instrumental settings for this inductively coupled plasma system (Boumans, 1978; Boumans and de Boer, 1975, 1977) has referred to the critical behaviour of the carrier gas flow. The carrier gas is used to transport the solution into the plasma; the carrier gas bores a tunnel into the centre of the toroidal-shaped plasma produced by the inductive heating. As the solution to be analysed is carried into this tunnel, the molecules are first dissociated into atoms or ions and then energy from the plasma excites the characteristic spectral radiation from the atomic or ionic species. The operating temperature of the plasma is high (around 6000 °K) but even at this temperature the majority of the atoms and ions remain in the ground state. Therefore small changes in the carrier gas flow can have a profound effect on the number of atoms emitting radiation.

Analytical performance

Before the results obtained with the system for individual elements are discussed a number of general features of the analytical performance are considered.

Detection limits. Several publications quote detection limits which can be achieved with ICP analysis; however, most of these are obtained under optimized conditions (i.e. using ultrasonic nebulization, optimum observation height, and the most sensitive lines, and using a monochromator system). Many of these quoted values are extremely low and do not relate to instrument performance under real operating conditions, where compromises in line selection and operating conditions must be made.

Table II gives the analytical lines used for the major and trace elements measured, and the detection limits as 3σ (standard deviations) *in the rock*, obtained using the Philips system under the compromise operating conditions, and using the $HF/HClO_4$ solution preparation method described above. The dissolution procedure used dilutes the rock 100 times, and it is therefore possible to judge from Table II the lowest concentration of an element which is measurable in solution. The detection limits for the major elements (Si, Al, Fe, Mg, Ca, Na, K, Ti, P, and Mn) are more than adequate for the levels it is normally required to measure (0.01 % or 100 ppm in the rock, 1 ppm in the rock solution), for all the elements except K. The sensitivity for K is just sufficient to allow this element to be measured down to 0.02 % in the rock but with the $LiBO_2$ fusion technique (where the dilution factor is 1:500) measurements of low levels of K in the rock (below 0.10 %) are not entirely satisfactory. For the trace elements measured sensitivities are sufficient to measure the elements down to below 10 ppm in the rock, and for some elements it is possible to measure concentrations at the 1 ppm level.

TABLE II. *Spectral lines used and trace element detection limits for ICP analysis of silicates*

Major element	Line (nm)	Trace element	Line (nm)	Detection limit (3σ)—ppm in rock
Si	251.61 (×2)	Zn	202.55	4
	288.16 (×2)	Ni	231.60	4.5
Al	308.22	Co	228.62	2
Fe	259.94 (×2)	V	290.88	4
Mg	383.83	Nb	309.42	3
Ca	315.89 (×2)	Cu	324.75	4.5
Na	588.995	Zr	339.20	3
K	766.49*	Y	371.03	5
Ti	337.28	La	398.85	4
P	213.62	Sr	407.77	5
Mn	257.61 (×2)	Ce	418.66	7
		Cr	425.44	5
		Ba	455.40	5
		Li	670.78	1
		Sc	361.38	1

Precision (reproducibility) and the use of an internal standard. Preliminary tests showed that the manufacturer's claim that precisions were better than 1–2 % were justified, and it became clear that precision would only be a significant problem for SiO_2, and to a lesser extent Al_2O_3, the most abundant oxides. Several detailed measurements were made over a period of several months for the precisions for these elements on rock solutions. These varied from 0.5 to 1.0 % relative standard deviation. Although this is better than many instrumental methods it is substantially worse than the precision attainable with XRF, and it was considered essential to improve on it.

A detailed analysis of the analytical noise of the ICP system showed that most (but not all) noise could be attributed to fluctuations in the amount of solution entering the plasma during the measurement. This can be demonstrated by observing the way the intensities for all the elements measured vary sympathetically, and by monitoring an argon line, the intensity of which moves in the opposite manner to element intensities; i.e. as more solution enters the plasma and element intensities increase, the argon line intensity decreases with less argon entering the plasma, and vice versa. The power delivered to the plasma was also monitored, but fluctuations (which were less than 0.2 %) did not correlate with short-term fluctuations in element intensities.

It is very probable that significant improvements in precision can be achieved by improvement to the peristaltic pump and the nebulizer system, and studies are currently in hand to do this. However, a substantial improvement in precision can be achieved by using an internal standard, as would be predicted in a system where variations in amount of solution are fluctuating. The choice of an element as an internal standard is complex. Lanthanum was used in this study, and, although it is not ideal, fluctuations in its intensity in the ICP system follow the two Si lines reasonably closely. Experience suggests that, provided the La internal standard is added carefully, the precision obtainable with ICP analysis of silicates can be reduced to less than 0.5 % for Si and Al using the internal standard method.

Interferences. There do not appear to be any significant chemical interferences in the ICP method. Chemical interferences which have been reported in atomic absorption work, i.e. the depression of the signal for Ca and Mg by Al and P or the interference by Al, Fe, Na, and other elements on Ti absorbance (Walsh, 1978) do not occur in ICP analysis. There are some small matrix effects: the addition of significant amounts of Na (1 % w/v) will change the signal for some of the elements by

TABLE III. *Spectral interferences for ICP in a silicate matrix*

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	Zn	Ni	Co	V	Nb	Cu	Zr	Y	La	Sr	Ce	Cr	Ba	Li	Sc	
wt.%																										
P_2O_5		**0.04**	0.01													**0.16**										
ppm																										A
Zn		5	3	**15**											14	6	1		2			1				
Ni			5								13		3							2					3	
Co			3					**80**				1											1			
V			3												16											
Nb		10		**15**				10						**107**												
Cu								13							15											
Zr																										
Y																										
La					**29**																					
Sr																							2			
Ce																	**36**	2								
Cr															24					13						
Ba														2			4			7					3	
Li								6																	25	
Sc								3													4					

Solutions were prepared containing the equivalent of 10% as the oxide for the major elements (for the $HF/HClO_4$ digestion sample preparation procedure where the dilution is 1:100) and 1000 ppm for the trace elements, and the interference intensities obtained were converted to concentrations. The horizontal columns against each element show which elements are subject to interference, and the vertical columns show which element causes that interference (e.g. the presence of 10% Al_2O_3 gives a reading equivalent to 0.04% on the P_2O_5 channel). No elements tested caused interference on the Si, Al, Fe, Mg, Ca, Na, K, Ti, and Mn channels.

A. Contributions to the elements (in ppm) from spectral interferences due to the presence of the elements at the head of the table. These elements were added in amounts equivalent to 10% of the oxide for the major elements and 1000 ppm for the trace elements. It is assumed that the interferences are linear.

approximately 2–10%. However, these are not serious if a similar matrix is used, and should present no problem for silicate analysis. The small extent of chemical interferences is demonstrated by the good straight-line calibration graphs obtained for almost all elements, with standard rocks of very different compositions.

The only significant interferences found are spectral interferences, line overlap for one element by another, or occasionally 'stray light', light scattered from a strong line inside the spectrometer. A complete table of spectral interferences for the analytical lines used in this study is given in Table III, and the magnitude of the interferences can be judged from the figures given. The values not only indicate the extent of the problems for this particular study, but should be of value in other comparable studies. It should be noted, however, that spectral interferences are influenced, amongst other factors, by the resolution of the spectrometer and of course line selection.

There are no significant interferences for the major elements in silicate rocks with the exception of P_2O_5, and for the trace elements the interferences are restricted to a small number of elements. Only the interference effects shown in heavy type are considered to be large enough to be worth correcting for, and this is done automatically in the computer recalculation of the results when output as concentrations.

Analytical results

ICP spectrometry is a solution method and results obtained for the elements in different matrices do not change substantially; it should therefore be possible to prepare calibration lines for the elements from entirely synthetic mixtures. However, it was decided initially to prepare calibration lines using existing standard rocks, and the US Geological Survey standard rocks, W-1, BCR-1, AGV-1, GSP-1, and G2 were used. Once prepared, these calibration lines (direct plots of known concentration against intensity) were loaded into the computer. The lines were entered as polygonal approximations, and they were updated with two reference points (high and low) during operation.

Fig. 2 shows comparisons between the ICP results and quoted values using the USGS and NIM standard rocks (quoted values from Flanagan, 1973) for the major elements Si, Al, Fe, Mg, Ca, Na, K, and Ti as oxides. This method of presenting the results is preferred to quoting new values for standard rocks to judge the accuracy of the method. The standard rocks represent a considerable range of silicate rock compositions and the excellent linear plots obtained demonstrate clearly the potential of this method of analysis.

In a further attempt to evaluate the accuracy of the ICP method of analysis for major elements under operational conditions, a suite of Tertiary granitic rocks from Mull was analysed. These rocks had previously been analysed by gravimetric, atomic absorption, and colorimetric methods (Walsh *et al.*, 1979). The comparisons between results can be evaluated from fig. 2, and it can be seen that for silicate rocks, especially the international rock standards, there is good agreement with published values.

Finally, and as an extreme test of the method, several minerals of widely differing compositions, which had previously been analysed by conventional methods, were all done with the $LiBO_2$ fusion method using only 100 mg of sample, and the ICP results given in Table IV are single determinations obtained as routine analyses. The results give some indication of the quality of the major element determinations which can be obtained without close matching of mineral matrix for standards and samples. The agreement between quoted and ICP results is not as close as that obtained for standard rock samples especially for some of the minor constituents (fig. 2, and Walsh, 1980; Brenner *et al.*, 1980); this may be due in part to the greater uncertainty in the quoted values for the minerals than for standard rock samples. It is noticeable that the Al_2O_3 values obtained are invariably lower by ICP than the quoted gravimetric values, and microprobe estimates of Al_2O_3 values in minerals also tend to give lower estimates than gravimetric determinations (Howie and Smith, 1966). Microprobe analyses are available for two of the orthopyroxenes in Table IV; for R62 microprobe analysis gave SiO_2 54.5, Al_2O_3 3.8, Fe_2O_3 10.9, MgO 30.7, CaO 0.2, TiO_2 0.1, MnO 0.3, and for A SiO_2 51.5, Al_2O_3 2.0, Fe_2O_3 25.9, MgO 20.9, CaO 0.4, TiO_2 0.1, MnO 0.5, and, with the exception of the Fe_2O_3 determination for A, the ICP results are closer to the microprobe results than the gravimetric values.

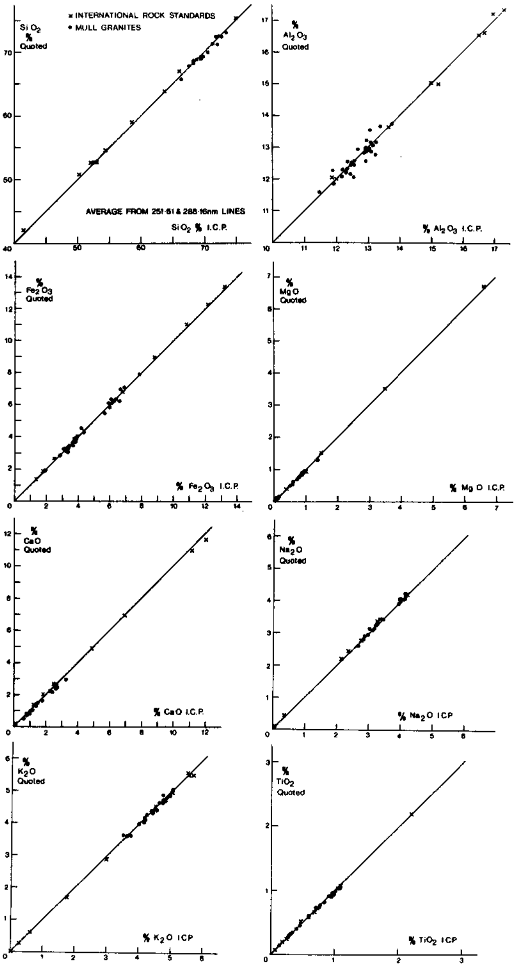

FIG. 2. Comparative plots for SiO_2, Al_2O_3, Fe_2O_3 (total), MgO, CaO, Na_2O, K_2O, and TiO_2. Comparisons are shown for international rock standards (quoted values from Flanagan, 1973) and selected granitic rocks from Mull, NW Scotland (quoted values from Walsh *et al.*, 1979).

Conclusions

Some previously published studies have referred to the use of an ICP system for silicate analysis (Burman *et al.*, 1977; Burman *et al.*, 1978; Walsh, 1980; Brenner *et al.*, 1980) and the comparison plots shown in fig. 2 demonstrate that for the major oxide constituents of silicate rocks the ICP source spectrometer is capable of giving results of entirely acceptable accuracy for geochemical work. The technique offers a number of identifiable advantages, notably the rapidity of analysis and the number of samples which can be handled in a normal working day. Some 30-40 complete analyses per hour are now being produced, allowing for instrument restandardization, and sample preparation is only slightly slower than XRF, for example. The mineral analysis comparisons in Table IV demonstrate that small samples of minerals can be analysed very rapidly, and the analyses also confirm that the method is inherently free from matrix effects. The calibration lines prepared for silicate rocks may be applied to a wide range of materials; it is, for example, possible to analyse carbonates without preparing different calibration lines.

The range of trace elements which are measured with the ICP system is quite adequate for most geochemical work, the only serious omission being

TABLE IV. *Comparison of ICP and published analyses of silicate minerals*

	Orthopyroxenes			Augites		Garnet	Olivine	K-feldspar	Plagioclase
	R62	CH113	A	4645	7286	3708	R62	3705	4642
SiO_2	53.8-53.63	50.4-50.05	51.4-51.45	49.3-49.74	50.8-50.32	37.4-37.20	39.5-39.76	64.6-63.58	58.2-58.10
Al_2O_3	3.63-4.53	3.78-4.08	2.18-2.59	5.37-5.02	2.73-2.84	21.02-21.75	0.03-0.10	18.52-19.57	26.01-26.44
Fe_2O_3*	11.31-11.62	29.57-31.24	23.59-25.74	6.92-7.21	13.67-14.89	35.35-37.71	15.55-15.94	0.35-0.56	0.52-0.21
MgO	30.45-30.31	17.21-16.51	21.12-21.20	14.15-14.42	11.47-11.53	4.74-4.82	44.61-45.12	0.15-0.05	0.05-0.03
CaO	0.36-0.53	0.25-0.46	0.46-0.65	22.18-23.51	20.04-20.65	1.33-1.53	0.02-0.10	0.25-0.40	8.51-7.84
Na_2O	0.01-0.02	0.04-0.09	0.01-0.02	0.04-0.15	0.48-0.49	0.02	0.02-0.01	1.48-1.56	6.53-6.48
K_2O	0.00-0.00	0.00-0.03	0.06-0.01	0.00-0.45	0.00-0.07	0.00	0.00-0.00	14.63-14.21	0.77-1.10
TiO_2	0.11-0.19	0.17-0.30	0.10-0.08	0.75-0.72	0.28-0.38	0.05-0.07	0.00-tr.	0.01-0.01	0.00
MnO	0.31-0.25	0.34-0.27	0.45-0.51	0.14-0.13	0.32-0.25	0.77-0.74	0.28-0.24	0.00	0.00-tr.
	ICP Q	ICP Q	ICP Q	ICP Q	ICP Q	ICP Q	ICP Q	ICP Q	ICP Q

* Total.

ICP—results obtained by routine analysis of 100-mg samples with inductively coupled plasma spectrometer.

Q —quoted values (classical/gravimetric values in Howie, 1955, 1958, 1963, 1964; Howie and Subramanian, 1957).

Rb. This element shows very low sensitivity in the high-temperature plasma, and the most sensitive line (780.02 nm) is beyond the wavelength range of the spectrometer used. Fortunately, it can be measured (on the solution prepared for ICP trace-element work) with a conventional flame photometer. On the other hand, ICP is not restricted to elements of atomic number greater than 9, and, unlike XRF, Li results are excellent. In addition, some elements (e.g. Sc, Co, V, and Ba) give very good agreement with known values for standard rocks and the method would appear to offer real improvements for these elements.

Finally, it may be noted that this paper describes only the results which are now being attained on the ICP system when used for routine silicate analysis after some eighteen months of operation. It is not unreasonable to suggest that further progress will substantially improve the method. Specifically, work already in progress suggests that the precision may be improved by minor mechanical improvements to the sample introduction system, e.g. installation of a more stable peristaltic pump. Refinements to the interelement (spectral) interference correction programme are continuing, and possibly most important for future applications is the use of the ICP system for the determination of the geochemically significant rare earth elements. It has already been demonstrated that rare earth element determinations can be made for several of these elements.

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