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Setting In-House XRF Reference Material for Minerals; A Case Study: Biotite Minerals of Malayer Granitoid Rocks (Western Iran)

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Abstract: To avoid of selecting an expensive and unavailable method for analyzing geological and mineral samples such as Inductively Coupled Plasma (ICP), Instrumental Neutron Activation Analysis (INAA), Electron Probe Micro-analyzer (EPMA) and etc. which waste the time and money we try to set an simple and fast analytical standard for X-ray Fluorescence Spectrometry (XRF). To get standards representative of the mineral samples, we select 15 typical samples from granitic rocks of Malayer granitoid complex Western Iran, separate their biotites, analyze them using ICP and use them as new standards. It is the only way to eliminate the matrix and other physical effects. The separated minerals are assessed as candidates for reference materials for major-element composition. These minerals are analyzed by ICP method in AMEDL laboratories, Australia and results are used for construction of calibration curves to XRF method at the Tarbiat Moallem University of Tehran in order to assess their performance as reference materials. Exactly the same samples are analyzed using new application by XRF. The results are very similar to those for ICP and demonstrated that this simple technic is effective.

Key words: Rock, calibration curve, reference materials, certificated reference materials

INTRODUCTION

The chemical compositions of rocks and minerals are used to solve numerous geological problems. Amounts of Fe, Al and Mg oxides in biotite used as record of tectonic and chemistry of generated magma. The X-ray fluorescence spectrometry (XRF) method is widely used to measure the elemental composition of rocks, soils and minerals. Standard Reference Materials (SRM) are constantly required in analytical facilities especially XRF to guarantee reliable analytical results. They play a pivotal role during the development of new analytical techniques, methodologies and new sample preparation procedures; for assessing short and long term stability of instrumentation; in detection of random and/or systematic errors during routine analysis; for cross-calibration of different analytical techniques and methodologies and in laboratory intercalibrations (Ingamells and Pitard, 1986).

Consequently, high-quality SRMs are one of the most valuable tools analytical facilities may possess, after the analytical instrumentation itself, but they are difficult to obtain as they are usually highly-priced and available in limited amounts. In the other hand, diversity and abundance of geological materials are the main preventing factor to develop SRMs and usually these standards are

limited to some major natural rocks and ores and many other rocks and minerals have not a self-standard.

Almost all analytical techniques for elemental analysis are calibrated by measuring the signal obtained from a set of calibration standards. The measured signal is then assumed to be a linear function of the concentration of the appropriate element in the standard. Quick and easy sample preparation, versatility of the instrumentation are just some of the reasons why XRF has become such a popular method of analysis across many geological investigations. The XRF analytical technique is far superior to ICP or Atomic Absorption because it is rapid and does not require extensive training or experience on the part of the analyst. The ICP method, for example, is an expensive and sample destructive method. In the other hand, since preparation of samples for XRF analysis is significantly faster and cheaper than most alternative methods; it is the most commonly used in mineral production. So, XRF is the technique of choice of most petrologists and geochemists to obtain rock, soil and mineral analyzes. High accuracy and precision and good to excellent detection limits across large parts of the periodic table are the other principal reasons for this choice. Mineral composition especially biotite can use as a indicator for crystallization history of igneous bodies,

nature of chemical weathering in various climates, processes of ore generation and many others. The chemical composition of biotite is classically used to estimate the conditions and source of their granitic host (Abdel-Rahman, 1994; Shabani *et al.*, 2003).

Natural rocks consist of several different minerals of highly variable composition and structure. This affects the behavior of X-rays in highly complex ways such as matrix effects, overlap effects, etc. In the other hand, the mineralogical composition of ores has been created millions of years ago and for analyzing them we have to reproduce the same mineralogical effects in standards and samples. To abstain of these harmful effects, the special standard are prepared for samples and monitor be refined by the analyst using calibration of a set of natural standards. To ensure reliable analyzes and compatibility of data from laboratories everywhere of the world agencies (i.e., United States Geological Survey (USGS), Geological Survey of Japan (GSJ), National Institute of Standards and Technology (NIST), French CRPG as provider of geological standards and etc. provide rock standards upon request. The USGS igneous rock standards were the first to be made universally available. Names of these original standards are very familiar to petrologists and geochemists (La Tour, 1989).

They have been analyzed many times by several worldwide labs and by many different methods. Descriptions of these standards, including the best values to date, addresses from which the standards may be obtained and etc. are published by Abbey (1983).

This study examines the performance of a new set of in-house multi-element standard for biotite. The data demonstrate how ours new standards deliver

accurate, precise and repeatable results for analysis of major and minor elements. Usage of this method provides a rapid tool to analyze samples and saves time and money.

MATERIALS AND METHODS

Geological setting, sample selection and preparation:

The Malayer granitoid complex, located 15 km Southwest of Malayer, in Western Iran (Fig. 1), is a part of the Sanandaj-Sirjan magmatic belt which forms during closure of Neothetys in the NW-SE direction. The age of these plutons is unknown but according to stratigraphic data it seems they formed due to orogenic activities in the Upper Cretaceous. These assemblages intruded into Jurassic schists and phillites and caused to a comprehensive contact metamorphism. Hornfels, hornfels schist and skarn are the results of this kind of metamorphism (Fig. 2). Intergrowth textures such as myrmekite and perthite, mylonitic granites, complex deformation and elongated shape imply injection of melt along the high-strain shear zone. This belt consist series of intrusive complex which extends from Uromiah lake in the Northwest to Bazman in the Southeast parallel to the entire length of the Zagros orogenic belt. The Malayer granitoid complex consists of various petrologic units including granite, granodiorite, diorite and gabbro as small to large plutonic bodies, widely distributed microgranite, aplite and pegmatite veins. They are emplaced in the high-strain shear zone (Ahadnejad *et al.*, 2008). The Malayer granitoid rocks are variably deformed and oriented (Fig. 3). This is revealed by orientation of feldspar and quartz and poorly separation of mafic and felsic minerals (Fig. 4).

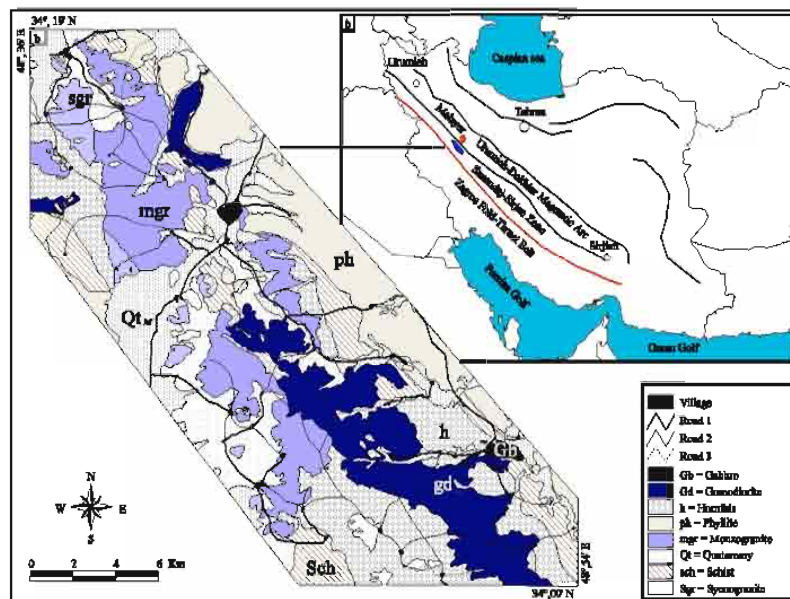


Fig. 1: Major geological units of Western Iran and location of (a) Malayer and (b) Malayer granitoids



Fig. 2: Formation of hornfels due to injection of granitic magma in the schist



Fig. 3: Foliation of biotite minerals in the granodiorite



Fig. 4: Photomicrograph of a biotite granite from Malayer granitoid complex Western Iran, (Bt = Biotite; K-f = K-Feldspar; Plg = Plagioclase; Qtz = quartz)

Table 1: Concentrations of major elements of separated biotites using ICP analyzes carried out in the AMDEL laboratory

Sample	Host rock	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	K ₂ O	Na ₂ O	TiO ₂	MnO	CaO	LOI	Total
V.11	Granite	32.85	22.84	17.83	7.620	11.250	0.12	2.31	0.20	0.18	3.74	98.82
V.13	Granodiorite	31.96	23.89	16.64	10.020	10.610	0.09	2.58	0.22	0.25	3.81	99.98
V.34	Granodiorite	31.84	23.81	16.58	10.250	10.550	0.06	2.71	0.24	0.38	3.61	99.97
V.42	Granodiorite	32.05	23.53	15.75	10.940	10.390	0.05	2.91	0.21	0.18	3.91	99.87
V.52	Granodiorite	32.51	22.98	16.43	9.480	11.050	0.09	2.17	0.21	0.45	3.70	98.98
V.68	Granodiorite	32.25	23.17	17.01	10.210	10.840	0.11	2.26	0.25	0.62	3.21	99.82
V.72	Granite	32.96	23.57	17.67	8.090	11.290	0.14	2.14	0.19	0.27	3.14	99.32
V.90	Granite	32.29	23.69	17.41	7.830	11.510	0.13	2.17	0.21	0.23	4.10	99.44
V.108	Granodiorite	31.92	24.12	16.55	10.110	10.670	0.11	2.83	0.26	0.49	3.01	99.96
V.122	Granite	31.98	23.55	16.77	8.170	11.340	0.12	2.44	0.20	0.22	3.94	98.73
V.131	Granodiorite	32.05	24.17	16.14	10.330	10.240	0.07	2.64	0.24	0.87	3.11	99.79
V.133	Granodiorite	31.78	23.84	16.29	10.450	10.330	0.10	2.48	0.26	0.41	3.87	99.71
V.153	Granodiorite	31.52	24.53	15.67	11.080	9.730	0.13	2.76	0.25	0.47	3.30	99.31
V.158	Granodiorite	32.58	20.94	16.33	10.670	10.410	0.11	3.01	0.21	0.91	4.05	99.11
V.163	Tonalite	29.91	24.83	16.08	10.870	10.080	0.12	2.68	0.26	1.10	4.15	99.96

The good exposure and wide distribution of felsic rocks in this region made it particularly suitable for such a geochemical study. Biotite is a common rock forming mineral for these granites. In this study, we selected 15 samples of these rocks and separated their biotites. They consist of a large amount of biotite that have a characteristic composition according to their geological conditions and host rocks. This is an important factor for geologists to determine granite types (S, I, A, M) and alteration effects on these rocks.

X-Ray Fluorescence (XRF) analysis of powdered samples, such as rocks, minerals and ceramics, has normally been carried out by several methods: i.e., the pellet (briquette) method (Tertian and Claisse, 1982; Feret and Jenkins, 1998; Matsumoto and Fuwa, 1979; Guevara and Verma, 1987) and the glass bead (fusion) method (Tertian and Claisse, 1982; Feret and Jenkins, 1998; Norrish and Thompson, 1990; Hua and Yap, 1994) for normal amounts of sample, or the filter cake method (Stankiewicz *et al.*, 1996) which consists in filtering the suspension of powder or precipitate, for small amounts of sample. The pressed pellet method has been widely used, because of its simplicity, rapidity and non-destructive nature. So we used this method for sample preparation.

The amount of sample necessary to give approximately 30 g of biotite was crushed to less than 1 inch diameter by using a jaw crusher and cone crusher. The crushed rock was then passed through a Fritsch disk pulverizer and sieved into four size fractions roughly the grain size of the mafic minerals (~75 micron, 200 mesh) so minerals would be released and a minimum of composite grains would remain. Each size fraction was washed in vertical-column water classifier. For most samples a rough biotite concentrate could be made by the classifier. The samples were dried by heating to less than 100°C under a heat lamp three times. Each washed and dried size fraction was passed through an electrostatic separator

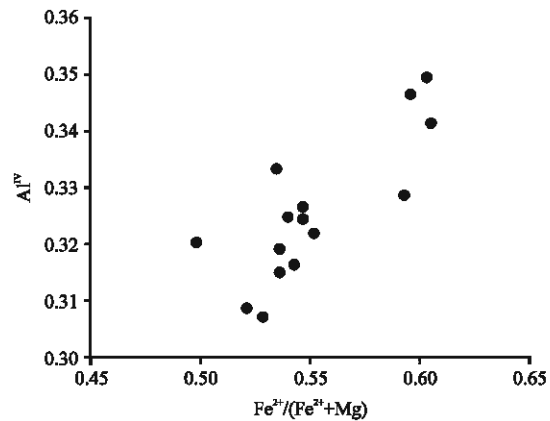


Fig. 5: Projection of the octahedral and tetrahedral sheet compositions expressed as $(Fe^{2+}/Fe^{2+} + Mg)$ and Al^{IV} , respectively

(Carpco M1H.13.111-5) set to give a rough biotite concentrate. Magnetic grains were removed from concentrates with a hand-magnet. Clean biotite concentrates were obtained by a combination of additional processes, including heavy liquid separations (using bromoform, tetrabromethane and diiodomethane) isodynamic (magnetic) separation and by rolling the concentrate down paper towels, electrostatically charged plastic sheets and finally, by hand-picking until an acceptable (about 99%) purity was obtained. The purified biotite concentrates were washed several times with acetone to remove traces of heavy liquids. The extracts of biotite are splitted in two sets: 20 g for ICP analyzes and 10 g for XRF analyzes. ICP analysis of minerals for multi-elements was performed in Australian Mineral Development Laboratories (AMDEL) as whole rock samples. The results, which will be used as reference, are shown in Table 1. According to the results, $Fe^{2+}/(Fe^{2+} + Mg)$ values are in the range from 0.5 to 0.6 (Fig. 5). The peraluminosity index (A/CNK) of biotite (1.48) is

considerably higher relative to that of the host rock (1.23). This confirms biotite as the most common mineralogical sink for excess aluminium in investigated granitic rocks. According to the composition of biotite on the Al_2O_3 vs. FeO_t diagram (Abdel-Rahman, 1994) the rocks belong to the peraluminous magmatic series (Fig. 6).

Instrumentation: The samples are weighed together with the binder with ratio 10:1. Subsequently the specimen is pressed with 12 ton pressure for one minute. MiniPress model PW4020/00 hydraulic press is used for pressing of sample powders. A PW2404 (Philips, Netherlands) wavelength dispersive type spectrometer (WDXRF) with a SuperQ software was operated with a Rh tube at a maximum 60 kV and 125 mA.

RESULTS AND DISCUSSION

By using of ICP analysis, we obtained the major element concentrations and used them as absolute

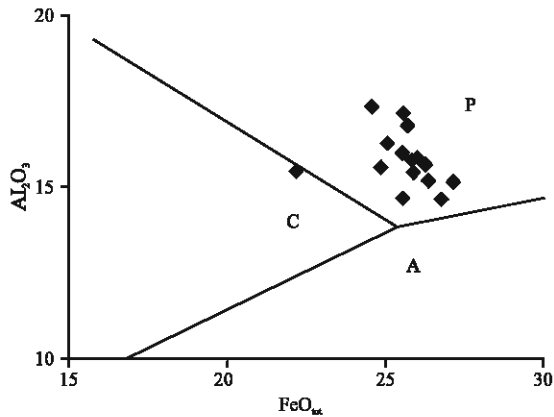


Fig. 6: Position of biotite in Al_2O_3 - FeO_{tot} (wt.%) diagram of Abdel-Rahman (1994). Fields of the discriminated granites, A: Alkaline; C: Calcalkaline; P: Peraluminous

Reference Material (RM). The following approach used for making a new standard; first, the channels and compound are defined, then the ICP values entered after that pellets was placed into a 37 mm in diameter steel sample holder and ran as a new standard. The Pulse Height Distribution (PHD) and check angle are employed for construction of calibration curves. The peak and background intensities of the elements were measured by using LiF200, PE and PX1 analyzing crystals and Duplex and Flow proportional counters as appropriate. The net intensities were calculated by subtracting the background intensities at the peak angles. All samples measured in comparison to a calibration curve. The results of XRF analysis are shown in the Table 2 and the comparison between both methods is shown in Fig. 5.

Under ideal conditions, the measured data would form an exact linear function of concentration. However, errors always occur on real data and the regression analysis, based on least square minimization, is used to calculate the best-fit calibration line. The calibration is therefore a plot of an independent variable (x), the concentration and a dependent variable (y), the analytical signal.

$$y = a+bx \tag{1}$$

Based on minimizing the sum of the squares of the differences

$$\sum_{i=1}^n (\hat{y}_i - y_i)^2 \tag{2}$$

where \hat{y} is the estimate of the analytical signal, derived for a specified concentration in the i-th calibration standard. Various indicators of the goodness of fit are available to assess the calibration data. One - and probably the most easiest to use - is the correlation coefficient calculated as

Table 2: Concentrations of major elements of separated biotites using XRF analyzes carried out in the Tarbiat Moallem University, Iran

Sample	Host rock	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	K ₂ O	Na ₂ O	TiO ₂	MnO	CaO	LOI	Total
V.11	Granite	32.65	23.01	17.81	7.590	11.470	0.13	2.28	0.21	0.16	3.74	99.050
V.13	Granodiorite	31.84	23.93	16.63	10.080	10.570	0.11	2.60	0.21	0.27	3.81	100.050
V.34	Granodiorite	31.81	23.86	16.52	10.240	10.510	0.07	2.64	0.21	0.41	3.61	99.880
V.42	Granodiorite	32.11	23.41	15.74	10.870	10.350	0.03	2.94	0.22	0.17	3.91	99.750
V.52	Granodiorite	32.52	22.94	16.51	9.470	11.080	0.07	2.19	0.19	0.47	3.70	99.140
V.68	Granodiorite	32.24	23.19	16.94	10.110	10.910	0.13	2.32	0.24	0.61	3.21	99.900
V.72	Granite	32.95	23.58	17.71	8.110	11.300	0.14	2.16	0.20	0.27	3.14	99.560
V.90	Granite	32.30	23.64	17.44	7.890	11.430	0.16	2.12	0.24	0.21	4.10	99.530
V.108	Granodiorite	31.94	24.12	16.52	10.130	10.590	0.13	2.87	0.25	0.47	3.01	100.030
V.122	Granite	32.01	23.58	16.71	8.200	11.320	0.14	2.45	0.21	0.22	3.94	98.780
V.131	Granodiorite	32.07	24.15	16.18	10.270	10.240	0.07	2.63	0.21	0.86	3.11	99.790
V.133	Granodiorite	31.79	23.85	16.27	10.440	10.340	0.11	2.41	0.25	0.39	3.87	99.720
V.153	Granodiorite	31.55	24.54	15.66	11.040	9.710	0.12	2.97	0.24	0.45	3.30	99.580
V.158	Granodiorite	32.56	20.92	16.31	10.680	10.410	0.12	2.97	0.22	0.97	4.05	99.210
V.163	Tonalite	30.01	24.91	16.07	10.840	10.040	0.11	2.54	0.27	1.04	4.15	99.980

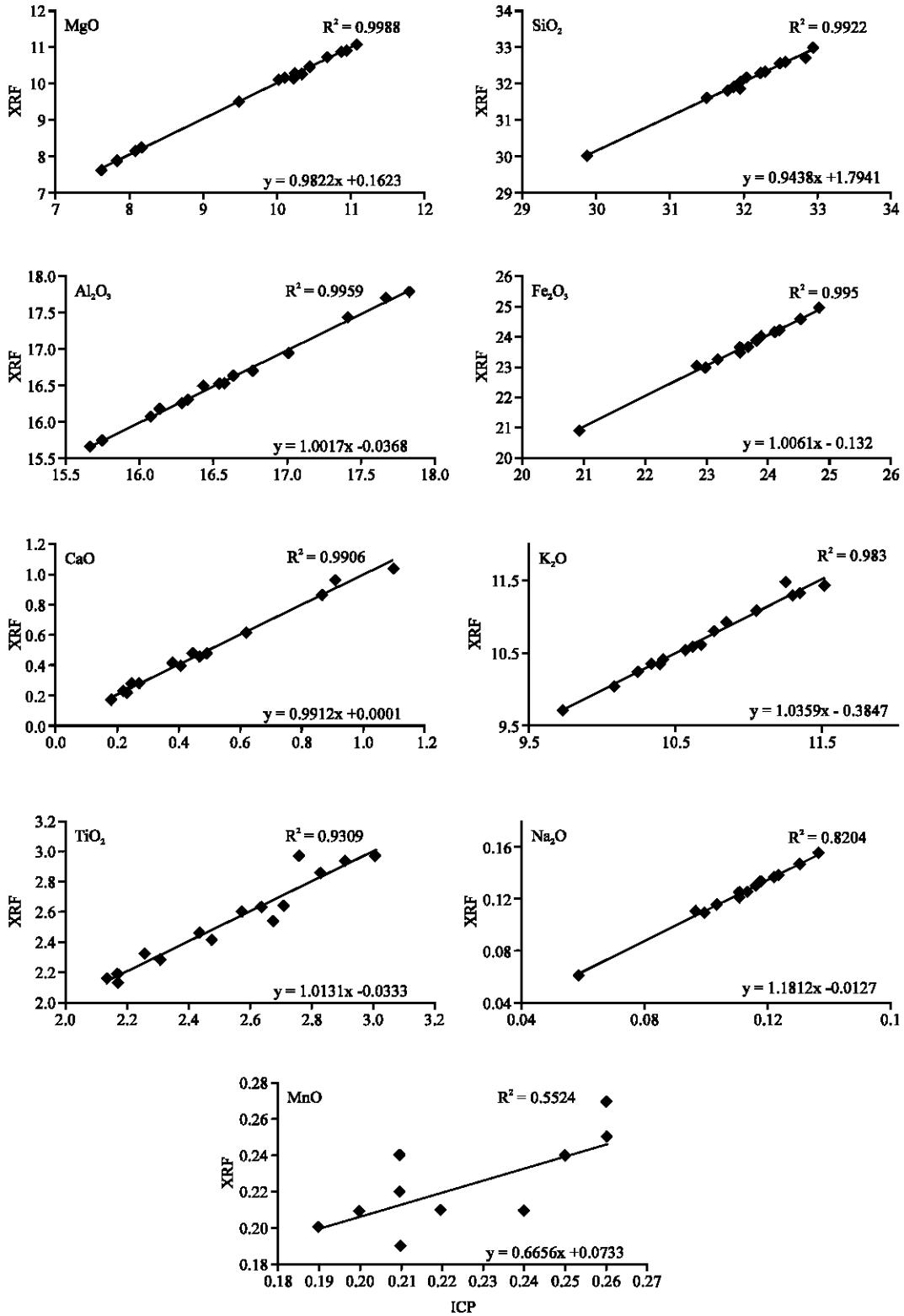


Fig. 7: Linear correlation of concentration results for ICP and in-house XRF standard

$$r = \frac{\sqrt{\sum_{i=1}^n (y_i - \bar{y})^2}}{\sqrt{\sum_{i=1}^n (\hat{y}_i - \bar{y})^2}} \quad (3)$$

For perfect fit $r = 1$ and for a good calibration data set $r > 0.98$, given a sufficient number of observations. In Fig. 7, we are plotted ICP and XRF results and shown correlation coefficient for these methods. Except to TiO_2 , MnO and Na_2O other elements have good agreement and $r \geq 0.98$. These indicate that these calibration lines could be reliable at least for those have $r \geq 0.98$.

CONCLUSIONS

In this study, preparation of new XRF standard procedure by using ICP method for geological samples has been evaluated. In general, WDXRF quantitative analysis is carried out by the calibration curves method. By mentioned procedure we have been obtained suitable calibration curves for major elements of biotite minerals. Using new calibration curves, palletized samples have been ran as unknown specimens. Concentration of elements in XRF has good agreement to those of ICP. The established quick and simple method can be used to any other minerals and rocks to get accurate analysis by XRF method.

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