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ON A SYSTEMATIC ERROR IN THE X-RAY DETERMINATION OF THE IRON CONTENT OF CHLORITES AND BIOTITES: A DISCUSSION

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ABSTRACT

A systematic error in the X-ray determination of the (Fe, Mg) content of biotites cannot be explained by inhomogeneous samples containing biotite crystals of various compositions (Gottardi, 1966). It is supposed that the curve of Franzini and Schiaffino (1963), calculated for members of the phlogopite-annite series, is not applicable to all biotites.

PROBLEM

In an investigation on the chemical composition of granitic, granodioritic and quartzdioritic rocks of the Cima d'Asta-Intrusion (Province Trento, North-Italy) Hörmann and Morteani (1966) determined the iron and magnesium contents of biotites by means of the X-ray methods reported by Gower (1957) and Franzini and Schiaffino (1963) and by chemical analysis. The Fe and Mg contents determined by X-ray intensity measurements were always about 20 percent higher than those found out by chemical analysis.

Starting from analogous observations in the determination of the Fe and Mg content of chlorites by X-ray methods, Gottardi (1967) suggested that this systematic error is caused by an occurrence of a population of biotites of different Fe contents within the investigated samples. According to him, the X-ray intensities of the 001 reflections of phlogopitic biotites are possibly reduced by the annitic biotites with relatively high mass absorption coefficients. Thus, a predominance of annitic biotites could be simulated. From the hypothetical origin of the Cima d'Asta-rocks (Hörmann and Morteani 1966) the occurrence of two biotite types seems possible:

(1) a relictic phlogopitic biotite, derived from assimilated basic rocks, and
(2) a more annitic type originated from the cristallisation of the granodioritic rocks.

For that reason the homogneity of the biotites samples studied by Hörmann and Morteani (1966) was investigated.

INVESTIGATIONS AND RESULTS

From the analyzed biotites (Hörmann and Morteani 1966) seven samples were selected covering nearly the whole observed (Fe, Mg) variation range. The samples 6, 7, 8 and 37 are biotites from quartzdioritic rocks, the samples 3, 4, and 8 from granodioritic ones. The sampling points are presented in Figure 2 of Hörmann and Morteani (1966). From each sample four homogeneous biotite crystals of 5 to 2 mg weight were taken. The X-ray intensities I_{004}, I_{005} and I_{006} of these crystals were measured and the $(I_{004}+I_{006}):I_{005}$ intensity ratios calculated (Table 1). Each value represents the arithmetic mean of four determinations. As indicated by the standard deviations, the intensity ratios of biotites from a single sample vary considerably within 3 to 13 percent. The arithmetic mean of the intensity ratio of biotite crystals of each sample corresponds well to that determined by Hörmann and Morteani (1966) using composite samples. (Table 1).

The Fe/Mg ratio was investigated by both X-ray intensity measurement and chemical analysis. Fe was determined by a spectrophotometric method (Yoe and Jones, 1944), Mg by atomic absorption spectrometry. The results are presented in Table 1. The Fe/Mg ratios of various biotite crystals from a single sample vary considerably, far beyond the analytical error, which is about ±2 percent. Fairly high variations have been found in the samples 4, 7, 8 and 37.

Discussion

From the results it is concluded:

1. The samples obviously contain biotites with different Fe/Mg-ratios. This confirms the supposed occurrence of various biotite types in the granodioritic and quartzdioritic rocks of the Cima d'Asta-Intrusion (Hörmann and Morteani, 1966). The differences in the Fe/Mg ratio explain also the formerly observed variation in birefringence and angle of the optical axes Hörmann and Morteani (1966).
2. The chemically determined Fe/Mg-ratios of the investigated biotite crystals show no distinct correlation to the corresponding X-ray intensity ratios $(I_{004}+I_{006}):I_{005}$ (Table 1). On the other hand, the average intensity ratios of the biotite crystals are definitely correlated to the Fe^N and Mg^N values calculated according to Franzini and Schiaffino (1963).

For the calculation of the Fe^N and Mg^N the biotite formulas of Hörmann and Morteani (1966) on composite samples were used. The use of the Fe^N and Mg^N calculated from the composite samples, is justified by the fact that the ratios of Fe/Mg and X-ray intensities of the composites are very similar to the corresponding average ratios of the biotite single crystals.

In any given amount of Fe^N, the intensity ratios of the biotites are always higher than those expected from the Franzini and Schiaffino-curve (Fig. 1). This is true of the Fe-rich and Mg-rich biotites of a single sample.

TABLE 1. Fe/Mg RATIOS OF BIOTITES FROM SEVEN QUARTZ-DIORITIC AND GRANITIC ROCK SAMPLES AS DETERMINED BY CHEMICAL ANALYSIS AND CORRESPONDING X-RAY INTENSITY RATIOS $(I_{004}+I_{006}):I_{005}$

Rock type	Sample no.	Fe/Mg ratios determined by chemical analysis			X-ray intensity ratios $(I_{004}+I_{006}):I_{005}$			
					Single crystals			Composite samples
		Ratio	Arith. mean	Standard deviation (%)	Ratio	Arith. mean	Standard deviation (%)	
Granodiorite	3a	2.42	2.35	4.7	2.11	2.15	7.9	2,2
	3b	2.22			2.40			
	3c	2.46			2.05			
	3d	2.30			2.05			
Granodiorite	4a	1.56	1.47	9.52	2.11	2.05	3.4	2,2
	4b	1.53			1.96			
	4c	1.54			2.11			
	4d	1.27			2.01			
Quartz-diorite	6a	1.13	1.15	8.7	1.88	1.77	7.3	1,7
	6b	1.22			1.69			
	6c	1.01			1.82			
	6d	1.23			1.68			
Quartz-diorite	7a	0.83	1.02	13.7	1.81	1.86	2.7	1.8
	7b	1.14			1.90			
	7c	1.12			1.91			
	7d	0.99			1.84			
Granodiorite	8a	1.40	1.24	8.7	1.63	1.92	13.0	1,6
	8b	1.19			1.80			
	8c	1.18			2.06			
	8d	1.18			2.19			
Quartz-diorite	35a	1.20	1.25	3.2	1.91	2.03	7.04	1,9
	35b	1.30			1.89			
	35c	1.24			2.18			
	35d	1.25			2.13			
Quartz-diorite	37a	0.92	0.95	17.8	1.80	1.70	5.3	1,6
	37b	1.06			.72			
	37c	1.11			1.58			
	37d	0.73			1.69			

On the above given grounds, Gottardi's assumption (Gottardi, 1966), that this systematic error is caused by an occurrence of a population of biotites of different Fe contents within the investigated samples could be refuted.

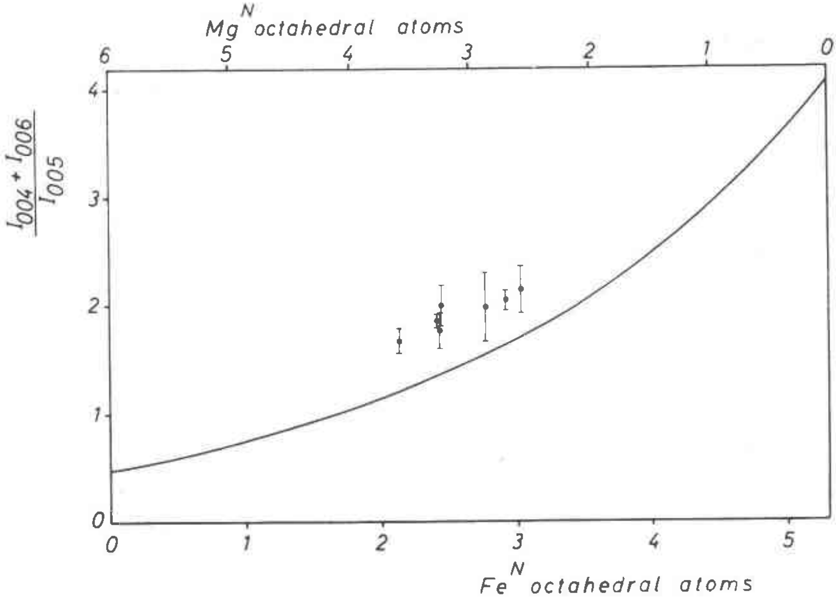

Fig. 1. Curve according Franzini and Schiaffino (1963) representing the intensity ratio ($I_{004}+I_{006}$):I_{005} as a function of the octahedral occupancy by Fe^N and Mg^N atoms. Measured intensities of the investigated biotites are plotted against the Fe^N calculated from biotite formulas (Hörmann and Morteani, 1966). The lines indicate the variation of the intensity ratios of various biotite crystals from the same sample. $Fe^N = Fe^{2+} + Fe^{3+} + Mn^{2+}$ (Franzini and Schiaffino, 1963).

The search for another reason of this error leads to the conclusion that one of the presuppositions made by Franzini and Schiaffino (1963) is not valid for biotites of these compositions. The Franzini and Schiaffino-curve was calculated for members of the phlogopite-annite series, assuming 0.7 octahedral vacancies in annite and 0.0 in phlogopite. This assumption might not be valid for the investigated biotites, and is possibly the main reason for the observed systematic error. The investigations will be continued.

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