Petrogenetic implications of the Fe^{3+} content of muscovite in pelitic schists

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Abstract

The Fe^{3+}/Fe^{2+} ratio of muscovite from typical metapelites is large. It reflects the opaque mineral assemblages in the rocks but appears to be independent of metamorphic grade. After correction for Fe^{3+}, the $Mg/(Mg + Fe^{2+})$ ratio is increased such that it affects any thermodynamic calculation. This study shows that a good approximation of the effects of Fe^{3+} on the $Mg/(Mg + Fe^{2+})$ ratio can be made by considering the opaque minerals present in a given sample. In other studies, the authors have shown the magnitude of similar approximations that can be made for the biotite of common metapelites. Hence, corrections for the effects of Fe^{3+} on $Mg/(Mg + Fe^{2+})$ ratios of these minerals can and should be routinely made when dealing with typical metapelites.

Introduction

Many previous studies have used the $Mg/(Mg + Fe^{2+})$ ratio of muscovite coexisting with various other minerals for geothermobarometry determinations (e.g., Kotov, 1975; Hynes and Forest, 1989; and Hoisch, 1989, 1990). Because complete chemical characterizations of these other minerals have not been available to workers, their $Mg/(Mg + Fe^{2+})$ ratios for muscovite were systematically in error—in some cases, significantly so. This paper demonstrates the magnitude of the effects of complete vs. incomplete analyses on such ratios. In particular, the opaque mineral assemblage has dramatic effects on the Fe^{3+} content of coexisting muscovite.

Unfortunately, the calibrations of geothermobarometers using muscovite $Mg/(Mg + Fe^{2+})$ ratios have been empirical in nature, and little information has been given for the opaque assemblages of the samples used for the calibrations. Hence, they need to be recalibrated taking into account the observations presented herein.

Methods of study

All mineral analyses were performed at the University of Maine on a MAC 400 electron microprobe in a single session using the same standards and analyst. Fe^{3+}/Fe^{2+} ratios were determined using Mössbauer spectroscopy for all but one sample (O-H-56), for which insufficient mineral separate could be obtained. We assumed that the sample had an Fe^{3+} content equal to the average of the other magnetite-bearing rocks. Where available, the bulk H data determined by U extraction and F contents analyzed by proton-induced γ-ray emission spectroscopy were also incorporated (Dyar et al., 1993). Unfortunately, dif-

ficulties in separation precluded our obtaining complete chemical characterization for all samples.

For each sample, the oxide data were recalculated (on a 24-O basis, if H_2O data are available; on a 22-O basis, otherwise) in two ways: (1) with the assumption of all Fe as Fe^{2+} and (2) using the Fe^{3+} data obtained by Mössbauer spectroscopy (Table 1). The results of the first approach are considered only in the text and shown in Figure 1.

Sample description

Two groups of samples are considered. One set, from metapelites described in Guidotti (1970, 1974), includes samples from graphite + ilmenite–bearing members of the Siluro-Devonian Rangeley stratigraphic sequence (Moench, 1971). The other set, from the Oquossoc area (Guidotti, 1977), collected a few kilometers from the first set, involves samples containing ilmenite + magnetite from the Dead River Formation (Osberg et al., 1985). All samples share the same metamorphic history and have comparable Al-, Si-, and Ti-saturating phases (Guidotti, 1978). Hence, the only fundamental difference between the two sets of samples is the opaque phase.

Results

Results are shown in Figures 1 and 2. In Figure 1, two sets of data are presented: circles are based on the Table 1 analyses; squares are based on formulas calculated with all Fe as Fe^{2+}. As the figure shows, if Fe^{3+} is not accounted for, the $Mg/(Mg + Fe^{2+})$ ratios can change by up to a factor of 2.0 or more for the magnetite-bearing rocks and 1.1–1.6 for the graphite + ilmenite rocks. It is noteworthy that the $Mg/(Mg + Fe^{2+})$ ratio remains approxi-

TABLE 1. Chemical analyses of muscovite based on microprobe and Mössbauer data

	Graphite + ilmenite–bearing rocks								
	Ra-D72-66	Ra-D37-66	Ra-A65-66	Ra-A69-66	Ra-B53-66	O-K-15	O-K-53	O-L-10	O-C-18
SiO_2	46.37	45.48	46.06	46.07	45.71	46.71	46.31	45.37	46.48
Al_2O_3	36.29	37.74	36.96	37.23	37.21	36.67	36.58	36.71	37.45
TiO_2	0.46	0.37	0.26	0.21	0.34	0.57	0.51	0.54	0.62
FeO	1.08	0.74	0.45	0.46	0.32	0.51	0.34	0.50	0.44
Fe_2O_3	0.47	0.39	0.39	0.27	0.43	0.55	0.60	0.56	0.60
MgO	0.38	0.50	0.33	0.28	0.36	0.36	0.36	0.29	0.28
Na_2O	0.57	0.75	1.74	2.15	1.52	1.45	1.63	1.47	1.15
K_2O	9.43	8.99	8.79	8.23	9.04	9.04	8.61	8.98	9.45
F	n.a.	n.a.	n.a.	n.a.	0.05	n.a.	0.05	0.05	0.04
H_2O	2.54	4.32	3.90	4.14	3.58	3.69	4.10	4.22	4.25
Total	97.58	99.27	98.87	99.05	98.53	99.54	99.06	98.66	100.74
XFe^{3+}	28	32	44	35	55	49	61	50	55
Si	6.378	6.038	6.164	6.127	6.161	6.229	6.171	6.084	6.106
[4]Al	1.622	1.962	1.836	1.873	1.839	1.771	1.829	1.916	1.894
[6]Al	4.264	3.945	3.996	3.965	4.076	3.994	3.919	3.889	3.907
Ti	0.048	0.037	0.026	0.021	0.034	0.057	0.051	0.054	0.061
Fe^{2+}	0.124	0.082	0.050	0.051	0.036	0.057	0.038	0.056	0.048
Fe^{3+}	0.048	0.039	0.040	0.027	0.044	0.055	0.060	0.056	0.059
Mg	0.078	0.099	0.066	0.056	0.072	0.071	0.071	0.058	0.055
[6]Total	4.563	4.202	4.178	4.121	4.262	4.234	4.139	4.112	4.131
Na	0.152	0.192	0.450	0.555	0.396	0.375	0.421	0.383	0.293
K	1.655	1.522	1.500	1.396	1.555	1.537	1.465	1.537	1.585
[12]Total	1.806	1.714	1.951	1.952	1.952	1.912	1.885	1.919	1.877
Cat. Tot.	14.369	13.916	14.129	14.072	14.213	14.146	14.024	14.032	14.008
F	0.000	0.000	0.000	0.000	0.021	0.000	0.021	0.021	0.017
H	2.331	3.825	3.482	3.673	3.219	3.282	3.645	3.775	3.724

Note: n.a. = not analyzed; wt% H_2O values are ±0.10 wt%; values for Fe^{3+}/Fe_{tot} are $\pm3\%$.
* This specimen also contains hematite.

mately the same in the two sample groups if the results are based on complete analyses. Apparently, this ratio is independent of the differences in the oxidation state implied by the two opaque assemblages. Although there is a two- to threefold increase of Fe_{tot} in the muscovite of the more oxidized samples, it has no effect on the Mg/$(Mg + Fe^{2+})$ ratio.

Figure 2 shows the relationship between [6]Al and Fe^{3+}. In graphite-bearing rocks, the trivalent substitutions are complex, and no direct relationship is discernible be-
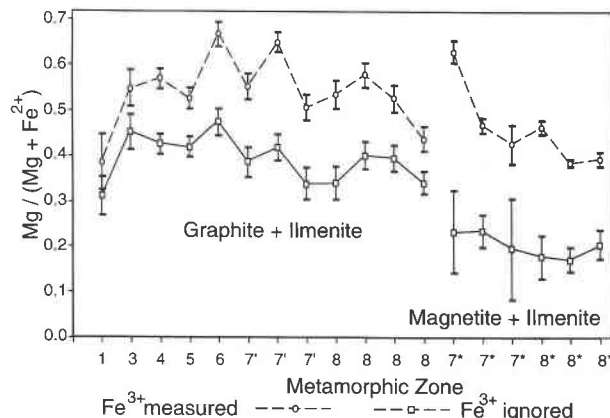
tween these two cations. However, when contrasted as a group vs. the magnetite-bearing rocks, direct substitution of Fe^{3+} solely for Fe^{3+} is clearly responsible for the decrease in [6]Al in the latter group (see Table 1 also). This observation also explains the constancy of the Mg/$(Mg + Fe^{2+})$ ratios discussed above.

CONCLUSIONS

Simple inspection of the data presented herein shows that errors will be inherent in any calculation involving muscovite for which all Fe is assumed to be Fe^{2+}. In the
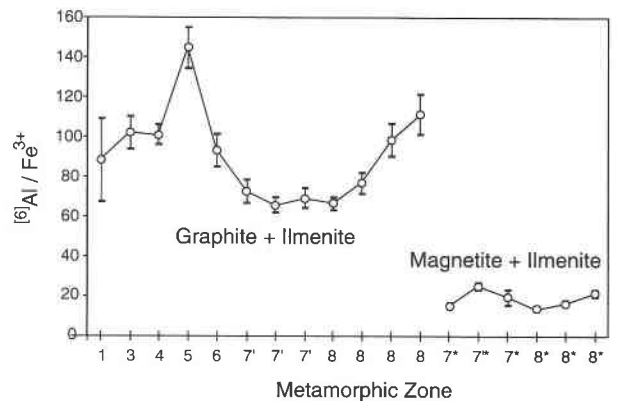

Fig. 1. A comparison of muscovite Mg/$(Mg + Fe^{2+})$ ratios when all Fe is assumed to be Fe^{2+} (squares) and when Fe^{3+} is subtracted (circles). Samples in zones 1–8 (lower garnet to upper sillimanite zones; see Guidotti, 1978, for a more complete description of zones) contain ilmenite + graphite. Samples in zones 7*–8* contain ilmenite + magnetite. Error bars represent 1σ.

Fig. 2. An illustration of the effect of Fe^{3+} content on the [6]Al content of muscovite in samples bearing graphite + ilmenite and magnetite + ilmenite. Symbols are as in Fig. 1. Error bars represent 1σ.

Table 1.—*Continued*

| Graphite + ilmenite–bearing rocks | | | Magnetite + ilmenite–bearing rocks | | | | | |
O-C-26	O-C-30	O-K-10	O-B-16*	O-G-92	O-I-1	O-H-72	O-H-56	O-H-49
46.15	46.54	46.04	45.66	45.88	46.59	46.92	45.84	45.99
36.66	37.27	37.48	35.00	36.15	35.60	34.52	35.72	36.22
0.65	0.60	0.74	0.56	0.34	0.65	0.91	0.83	0.61
0.45	0.52	0.65	0.49	0.74	0.86	0.82	0.98	1.06
0.52	0.40	0.36	2.49	1.52	1.94	2.72	2.22	1.76
0.34	0.32	0.28	0.46	0.36	0.36	0.39	0.34	0.38
1.11	1.03	0.96	1.33	1.36	1.17	0.68	0.89	0.98
9.20	9.41	9.55	9.00	9.09	9.26	9.47	9.54	9.38
0.05	0.05	0.06	0.07	0.03	0.04	0.04	0.04	0.06
3.69	4.11	3.92	3.71	n.a.	n.a.	n.a.	n.a.	n.a.
98.79	100.24	100.01	98.73	95.46	96.44	96.45	96.38	96.42
51	41	33	82	65	67	75	67	60
6.201	6.143	6.111	6.211	6.094	6.142	6.208	6.074	6.070
1.799	1.857	1.889	1.789	1.906	1.858	1.792	1.926	1.930
4.008	3.943	3.977	3.825	3.756	3.677	3.593	3.654	3.708
0.065	0.060	0.074	0.057	0.034	0.064	0.090	0.082	0.060
0.050	0.058	0.072	0.056	0.082	0.095	0.090	0.109	0.117
0.052	0.040	0.036	0.255	0.152	0.192	0.271	0.221	0.175
0.068	0.064	0.056	0.094	0.071	0.070	0.078	0.068	0.075
4.244	4.164	4.215	4.286	4.095	4.098	4.123	4.134	4.135
0.289	0.264	0.246	0.350	0.351	0.298	0.174	0.227	0.252
1.576	1.584	1.617	1.562	1.541	1.558	1.598	1.613	1.579
1.865	1.848	1.863	1.912	1.892	1.856	1.773	1.840	1.831
14.109	14.012	14.078	14.198	13.987	13.954	13.895	13.974	13.966
0.021	0.021	0.025	0.030	0.013	0.017	0.017	0.017	0.025
3.307	3.619	3.471	3.367	0.000	0.000	0.000	0.000	0.000

graphite-bearing rocks, the Mg/(Mg + Fe^{2+}) ratio is systematically in the range of about 0.1 too low when Fe^{3+} is not considered. For magnetite-bearing rocks, the error in the ratio is at least 0.2. The results presented here are only a small subset of our data set, but they provide good approximations for the corrections for Fe^{3+}, which should be applied routinely to data sets from pelitic schists: for graphite-bearing samples, the average Fe^{3+}/Fe$_{tot}$ ratio of muscovite is 0.45 ± 0.11; for the magnetite-bearing samples, the ratio is 0.67 ± 0.06. Our results also show the magnitude of the correction that should be used in any thermodynamic treatment that includes the Mg/(Mg + Fe^{2+}) ratio of such muscovite. Other studies by Dyar (1990) and Guidotti and Dyar (1991) have shown the magnitude of similar correlations that should be applied to biotite from typical metapelites. For both muscovite and biotite, these are first-approximation corrections in that they do not include any consideration of site assignments, vacancies, etc.

Nonetheless, the Fe^{3+} data are now sufficiently well established for both the biotite and the muscovite of typical metapelites that there is no reason for authors doing geothermobarometry calculations not to assume the validity of the above-described corrections and use them on a routine basis.

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