Estimating the Mg# and Al^{VI} content of biotite and chlorite from shortwave infrared reflectance spectroscopy: Predictive equations and recommendations for their use

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A B S T R A C T

Shortwave infrared (SWIR, 1000–2500 nm) reflectance spectra of biotite and chlorite were investigated to establish quantitative relationships between spectral metrics and mineral chemistry, determined by electron microprobe analysis (EMPA). Samples spanning a broad range of mineral compositions were used to establish regression equations to Mg#, which can be estimated to ± 3 and ± 5 Mg#, and to Al^{VI} content, which can be estimated to ± 0.044 Al^{VI} (11 O) and ± 0.09 Al^{VI} (14 O), respectively for biotite and chlorite. Both minerals have absorptions at common positions (1400, 2250, 2330 nm), and spectral interference may occur in mineral mixtures. For an equivalent Mg#, absorptions of chlorite are offset to 1–15 nm higher wavelengths relative to those of biotite. If the incorrect mineral is identified, errors in the estimation of composition may occur. Additionally, the 2250 nm absorption, which is related to Al(Mg,Fe)-OH in both minerals, is strongly affected by both the Al^{VI} content and Mg#. This can lead to erroneous Mg# estimations in low Al^{VI} samples. Recommendations to mitigate these issues are presented.

1. Introduction

Biotite and chlorite are ubiquitous alteration products in numerous types of hydrothermal ore deposits (MacLean and Kranidiotis, 1987; Sillitoe, 2010). Broad mineralogical zonations can often be defined around hydrothermal centers, and, if correctly recognized as such, can be used to target mineralized areas. In many instances, within each mineralogical zone, the chemistry of a given mineral also varies with alteration intensity. For example, biotite and chlorite in porphyry deposits (Selby and Nesbitt, 2000; Wilkinson et al., 2015), and chlorite in VMS deposits (MacLean and Kranidiotis, 1987) vary in composition with distance to mineralization, and can provide more refined vectors towards mineralization than mineralogical zonations.

Shortwave infrared (SWIR, 1000–2500 nm) reflectance spectroscopy is now commonly used to identify mineralogy in and around mineral deposits, either in the form of point data acquired using portable instruments (e.g., Biel et al., 2012; Harraden et al., 2013), or in the form of hyperspectral imagery acquired using lab-based or airborne hyperspectral sensors (e.g., Laakso et al., 2015; Dalm et al., 2017; van der Meer et al., 2018). Biotite and chlorite absorption positions are often used as proxies to qualitatively describe mineral composition, for example inferring Mg, Mg-Fe, or Fe-rich biotite or chlorite (e.g., Jones

et al., 2005; Laakso et al., 2015). Conventional economic geology studies, on the other hand, report precise mineral compositions for given alteration zones. For example, Selby and Nesbitt (2000) report altered biotite in a porphyry-Cu deposit at Mg# 60–75, and background biotite around Mg# 45. Direct links between qualitative compositions derived from hyperspectral data and quantitative mineral compositions in existing studies are therefore difficult to establish, especially in instances where compositional changes are subtle (e.g., < 15 Mg#).

For biotite, this stems from the lack of availability of quality regressions between mineral chemistry and SWIR responses. For chlorite, the displacement of absorption positions as a function of Mg# has been partially investigated, with descriptions and regressions reported in McLeod et al. (1987) and King and Clark (1989), but the effect of Al^{VI} content, which strongly influences the spectral response of chlorite, has not been characterised.

The primary goal of this study is therefore to refine the relationships between mineral chemistries (here Mg# and Al^{VI} content) and SWIR responses of biotite and chlorite, which to date exist in a mostly qualitative nature. Calibrated regressions are provided for all absorptions of these two minerals, some of which were not previously reported. For the absorptions that have previously been investigated, improvements in the precision of the regressions are presented, and will allow

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Table 1
Source and composition of biotite (apfu for 11 O) determined from EMPA.

Sample	Type/Source	Mg#	Si	Al^{IV}	Al^{VI}	Mg	Fe	Ti	Cr	Mn	Ca	Na	K
Bt-8	Crystal (Unk.)	28.4	2.76	1.24	0.26	0.68	1.72	0.15	<0.01	0.03	<0.01	0.01	0.97
Bt-9	Crystal (Bancroft)	60.4	2.98	1.02	<0.01	1.65	1.08	0.13	<0.01	0.03	<0.01	0.05	0.95
Bt-12	Crystal (Bancroft)	59.7	2.98	1.02	<0.01	1.61	1.09	0.13	<0.01	0.06	<0.01	0.08	0.91
Bt-13	Crystal (Unk.)	28.4	2.76	1.24	0.25	0.68	1.72	0.16	<0.01	0.03	<0.01	0.01	0.97
Bt-14	Crystal (Unk.)	82.4	3.01	0.99	0.01	2.35	0.50	0.07	<0.01	0.01	<0.01	0.07	0.92
Bt-15	Crystal (Unk.)	70.5	2.95	1.05	<0.01	1.97	0.82	0.11	<0.01	0.02	<0.01	0.06	0.92
Bt-16	Crystal (Unk.)	58.9	2.98	1.02	<0.01	1.59	1.11	0.13	<0.01	0.06	<0.01	0.08	0.93
Phl-1	Crystal (Unk.)	99.0	2.99	1.01	0.02	2.94	0.03	<0.01	<0.01	<0.01	<0.01	0.19	0.79
Phl-2	Crystal (Unk.)	93.7	3.02	0.98	0.04	2.72	0.18	0.02	<0.01	<0.01	<0.01	0.04	0.95
Phl-3	Crystal (Unk.)	93.7	2.90	1.10	0.11	2.62	0.18	0.04	<0.01	<0.01	<0.01	0.02	0.96
Phl-5	Crystal (Unk.)	92.5	2.91	1.09	0.11	2.59	0.21	0.05	<0.01	<0.01	<0.01	0.02	0.96
Phl-6	Crystal (Unk.)	93.4	3.02	0.98	0.03	2.73	0.19	0.01	<0.01	<0.01	<0.01	0.03	0.95
Phl-7	Crystal (Unk.)	86.9	2.79	1.21	0.17	2.38	0.36	0.06	<0.01	<0.01	<0.01	0.09	0.87
Phl-8	Crystal (Unk.)	94.2	2.89	1.11	0.09	2.68	0.17	0.04	<0.01	<0.01	<0.01	0.04	0.94
P0111	Metased. (Malartic)	72.8	2.88	1.12	0.25	1.82	0.68	0.09	<0.01	0.01	<0.01	0.01	0.94
P0122	Metased. (Malartic)	88.1	2.92	1.08	0.26	2.22	0.30	0.06	0.02	<0.01	<0.01	0.01	0.93
P0906	Metased. (Malartic)	81.6	2.91	1.09	0.24	2.07	0.47	0.07	0.01	0.01	<0.01	0.01	0.96
P0907	Metased. (Malartic)	75.4	2.87	1.13	0.22	1.92	0.63	0.08	0.01	0.01	<0.01	0.01	0.95
K389048	Metased. (Malartic)	62.8	2.80	1.20	0.29	1.56	0.92	0.09	0.01	0.02	<0.01	0.01	0.91
K389056	Metased. (Malartic)	72.7	2.86	1.14	0.27	1.82	0.68	0.09	<0.01	0.01	<0.01	0.01	0.91
K389084	Metased. (Malartic)	54.3	2.77	1.23	0.31	1.35	1.14	0.09	0.01	0.02	0.01	0.02	0.87
K389090	Metased. (Malartic)	56.0	2.77	1.23	0.28	1.38	1.09	0.11	0.01	0.01	<0.01	0.01	0.89
K389202	Metased. (Malartic)	91.7	3.01	0.99	0.15	2.47	0.22	0.04	0.01	0.01	0.01	0.01	0.91
K389203	Metased. (Malartic)	90.6	3.03	0.97	0.09	2.52	0.26	0.04	<0.01	0.01	<0.01	0.01	0.93
K389208	Metased. (Malartic)	57.5	2.81	1.19	0.28	1.42	1.05	0.11	<0.01	0.02	<0.01	0.01	0.93
Representative sample		Total	SiO2	Al2O3		MgO	FeO	TiO2	Cr2O3	MnO	CaO	Na2O	K2O
Bt-16		92.96	38.28	11.03		13.67	17.01	2.22	0.03	0.88	0.01	0.51	9.34

Assumes all Fe as Fe^{2+}. Al^{IV} and Al^{VI} are calculated assuming full occupancy of the T-sites. Mg# is calculated as Mg/(Mg + Fe). Raw data are available in the supplementary material.

hyperspectral studies to link estimated mineral compositions to precisely measured compositions as produced by conventional economic geology studies. Finally, pitfalls that can be encountered in the use of such regressions are identified (e.g. in mineral mixtures), and recommendations are made to minimize errors in the prediction of composition.

2. Background

2.1. Mineral chemistry of phyllosilicates

In biotite ($K(Mg,Fe)_3[AlSi_3]O_{10}(OH)_2$) and chlorite (($(Mg,Fe)_5Al$ $[AlSi_3]O_{10}(OH)_8$), mineral chemistry can vary significantly from end-member composition. The main chemical changes occur for the M-site cations (in the octahedral layer), resulting from two substitution mechanisms; simple Mg↔Fe substitution, and a coupled Tschermak substitution (Al^{IV}Al^{VI}↔Si,(Mg,Fe)) (Bailey, 1986; Fleet et al., 2003; Deer et al., 2009). Shortwave infrared absorption features observed in reflectance spectra are caused by OH^- groups that are directly bound to the octahedral layer (Farmer, 1968; Hunt, 1977; Clark et al., 1990), and are therefore influenced by its composition.

2.2. Hydroxyl absorption features in the SWIR

For biotite, numerous studies have investigated the effects of mineral chemistry on reflectance spectra, but focus has been on the longer wavelengths (above 2500 nm, 40–4000 cm^{-1}, Vedder, 1964; Redhammer et al., 2000; Beran, 2002). In the SWIR, Post and Crawford (2014) showed a correlation between increasing FeO wt% (although they did not provide complete compositional data) and the increasing position of the 1390 nm absorption. The 2250 nm absorption is known to occur only in the presence of octahedral Al (Post and Noble, 1993), and although it is at times erroneously referred to as the biotite/chlorite "Fe-OH" absorption (Sun et al., 2001; Jones et al., 2005), it is assigned to Al(Mg,Fe)-OH (Besson and Drits, 1997; Martinez-Alonso et al., 2002;

Bishop et al., 2008). The 2330 and 2390 nm absorptions are assigned to Mg-OH (Clark et al., 1990). Although correlations between composition and absorption positions are known to exist for the fundamental absorptions (> 2500 nm), no such correlations have been quantitatively described for most absorptions in the SWIR.

For chlorite, because OH^- groups occur in additional M-sites (in the hydrated octahedral interlayer), its SWIR spectrum shows more absorptions than that of biotite. Main absorptions occur at 1400, 2250 and 2330 nm, and weaker absorptions occur near 1450, 1550, 2000, 2290, 2350 and 2400 nm. McLeod et al. (1987) reported a shift in wavelength of the main absorptions from 1385 to 1410 nm, 2245–2265 nm and 2320–2365 nm, for high to low (molar) Mg# respectively. King and Clark (1989) also indicated a correlation with Mg#, and provided high resolution spectra of the OH^- overtone region. More recently, Bishop et al. (2008) reported an Al(Mg,Fe)-OH absorption at 2248 nm for clinochlore (Mg# 88) and 2261 nm for chamosite (Mg# 23), which matches the previously reported data. However, no link has been made to variations with Al^{VI} content, which strongly influences the strength and position of absorptions observed in spectra of chlorite.

3. Methodology

3.1. Sample suite

A total of forty-six crystals or rock samples rich in a mineral of interest were selected for acquisition of infrared (IR) spectra, measured from 1000 to 2500 nm. Electron microprobe analysis (EMPA) data were acquired on corresponding polished grain mounts (crystal samples) or polished thin sections (rock samples).

For biotite (Bt), fourteen crystals from unknown localities (except Bt-9 and Bt-12 which are from Bancroft, Ontario, Canada) and eleven rock samples were analysed. The crystals ranged in size from 5 mm to 5 cm wide sheets, and were generally < 1 mm thick. The rock samples were biotite-rich greywackes from the Pontiac Group metasediments, near the town of Malartic, Quebec, Canada. In these samples, biotite