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Spectral characteristics of propylitic alteration minerals as a vectoring tool for porphyry copper deposits



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ABSTRACT

Short-wave infrared (SWIR) reflectance spectroscopy is a quick and effective method of detecting and characterising hydrothermal alteration associated with ore deposits, and can identify not only mineral species but also changes in the major element composition of minerals. Porphyry deposits represent large accumulations of valuable metal in the Earth's crust and have extensive alteration signatures making them an attractive target for exploration, particularly by remote sensing which can cover large areas quickly. Reflectance spectroscopy has been widely applied in sericitic (phyllic), argillic and advanced argillic alteration domains because it is particularly effective in discriminating bright clay minerals. However, the propylitic domain has remained relatively unexplored because propylitic rocks are typically dark and produce relatively poorly-defined spectra.

This study utilised an ASD TerraSpec 4 handheld spectrometer to collect SWIR spectra from rocks surrounding the Batu Hijau Cu-Au porphyry deposit in Indonesia, where previous work has identified systematic spatial variations in the chemistry of chlorite, a common propylitic alteration mineral. Spectra were collected from 90 samples and processed using *The Spectral Geologist* (TSG) software as well as the *Halo* mineral identifier to characterise mineralogy and extract the positions and depths of spectral absorption features, which were then correlated with major element geochemistry. Two diagnostic chlorite absorption features located at around 2250 nm and 2340 nm correlate with the Mg# (Mg/[Mg + Fe]) of chlorite, both in terms of wavelength position and depth. As the Mg# increases, the wavelengths of both features increase from 2249 nm to 2254 nm and from 2332 nm to 2343 nm respectively, and absorption depths also increase significantly. In the spatial dimension, these feature variations act as reasonably strong vectors to the orebody, showing systematic increases over a transect away from the porphyry centre, peaking at distances of around 1.6 km, which matches the spatial trend displayed by Mg#, as well as various trace element indicators in chlorite. The hull slope in spectra between 1400 nm and 1900 nm is also shown to increase with Mg#, and the position of an absorption feature at 1400 nm increases with the Al:Si ratio, a parameter that also tends to increase with proximity to porphyry deposits.

Feature depth variations in particular appear to represent a new finding in chlorite reflectance spectroscopy; however, the causes are not entirely clear and require further investigation. Nonetheless, the systematic behaviour provides a potentially useful new tool for exploration in propylitic alteration zones.

1. Introduction

Porphyry deposits represent some of the largest accumulations of metal in the Earth's crust and are the primary source of the world's Cu and Mo, and an important source of Au and other metals (Sillitoe, 2010). Deposits are formed as a result of hydrothermal fluids that exsolve from intrusive magmatic bodies, precipitating metals into the surrounding rocks. The outward movement of these hydrothermal

fluids creates distinct alteration zones recognised by the occurrence of specific mineral assemblages (Sillitoe, 2010; Cooke et al., 2014a). The propylitic alteration zone represents the most distal signature of mineralisation, detectable kilometres away from the main orebody (Cooke et al., 2014a) and, as such, is an important target for exploration. Alteration zoning is not only expressed in mineralogy, but in whole-rock and mineral geochemical trends which can act as vectors towards orebodies (e.g. Emmons, 1927; John, 1978; Norman et al., 1991; Cooke

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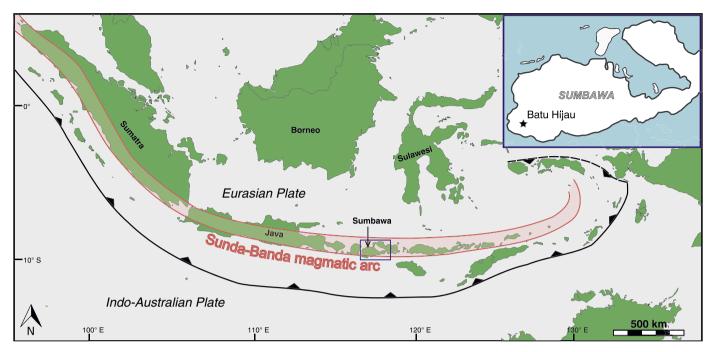


Fig. 1. Principal tectono-magmatic features of Indonesia. The major subduction zone is shown as well as the Sunda-Banda magmatic arc. Subduction of the Indo-Australian plate beneath the Eurasian plate produces the calc-alkaline magmatism that characterises the Cenozoic Sunda-Banda arc. Batu Hijau is located on the island of Sumbawa in the south-west (inset map). Modified after Garwin et al. (2005).

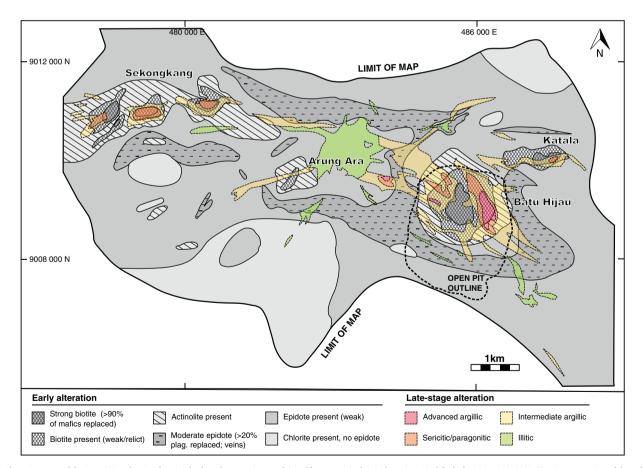


Fig. 2. Alteration map of the Batu Hijau district showing both early-stage (greyscale) and late-stage (colour) alteration. Modified after Garwin (2000). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Technical specifications of the TerraSpec 4 spectrometer and Hi-Brite Contact
Probe accessory that were used to collect infrared-spectra (ASD Inc., 2015).

Wavelength range	350-2500 nm
VNIR detector	(350-1000 nm) 512 element silicon array
SWIR 1 & 2 detectors	(1001-1800 nm) & (1801-2500 nm) Graded Index
	InGaAs Photodiode, TE Cooled
Spectral resolution	3 nm (VNIR range)
(smallest detectable absorption feature)	10 nm (SWIR 1 & 2 range)
Wavelength accuracy	0.5 nm
Signal-to-noise ratio	9000:1 (VNIR & SWIR 1 range)
	4000:1 (SWIR 2 range)
Number of channels	2151
Acquisition software	Indico® Pro
Hi-Brite Contact Probe	
Light source	Halogen bulb, 2901 °K (\pm 10%)
Spot size	10 mm

et al., 2014b; Wilkinson et al., 2015).

Remote sensing is a valuable tool in mineral exploration, providing a quick way to identify and map hydrothermal alteration products over large areas. Much work has been done on characterising the hydrothermal alteration associated with ore deposits in terms of spectral signatures (Yang and Huntington, 1996; Herrmann et al., 2001; Sun et al., 2001; Jones et al., 2005) including porphyry deposits specifically (Cudahy et al., 2001; Chang et al., 2011; Dilles, 2012; Zadeh et al., 2014; Halley et al., 2015). However the focus of these studies is on the clay-dominated, argillic and sericitic alteration assemblages. In relation to a particular exploration application, Chang et al. (2011) showed that it is possible to use spectral features of alunite in the advanced-argillic alteration zone as pointers towards porphyry ore deposits.

Investigations into the SWIR spectroscopy of chlorite and epidote, two of the most prevalent propylitic alteration minerals, are few. However, sensitivity of SWIR spectra to mineral chemical changes that are recognisable both in the laboratory (King and Clark, 1989; Liebscher, 2004; Bishop et al., 2008) and in hyperspectral imaging (Cudahy et al., 2001; Roache et al., 2011) have been recognised. This indicates that spectral characteristics might be able to act as a vector to orebodies in the propylitic domain as well as the more proximal alteration zones.

The large footprint of propylitic alteration should present an attractive target for remotely sensed mineral exploration. However, the rocks that typify propylitic alteration zones are often dark (low reflectance) making their characterisation exceedingly difficult. Fortunately, the availability of increasingly sensitive portable field spectrometers has opened up the possibility of tackling this problem. These spectrometers are an ideal tool for detailed investigations into the spectral features of rocks; they can produce high-resolution spectra, free from the effects of atmospheric scattering and absorption, and have absorption features clearly detectable even at reflectance values as low as 1%.

This study utilised an ASD TerraSpec 4 spectrometer to collect infrared spectra of rocks from the Batu Hijau porphyry copper system in Indonesia. It builds on previous research done as part of the AMIRA P765A research project (AMIRA International Ltd., 2008) which included studies of spatial variation in the geochemistry of chlorite (Wilkinson et al., 2015) and epidote (Cooke et al., 2014b). Most importantly, the work utilised the same samples analysed by Wilkinson et al. (2015) so that extensive prior knowledge of whole-rock geochemistry and mineral chemistry was available. The primary aims were to characterise the infrared spectra of propylitic rocks throughout the

Batu Hijau alteration footprint, and to identify any spectral features that might reflect systematic geochemical variation in the spatial domain which could therefore act as vectors towards economic mineralisation. Longer term, it is hoped that such features could be targeted by airborne hyperspectral or even satellite remote sensors, such as ASTER or WorldView-3, allowing a relatively quick way to search large areas of propylitic alteration for contained porphyry deposits.

2. Background geology

Batu Hijau is a giant Cu-Au porphyry deposit located in the southwestern part of Sumbawa island, Indonesia (Fig. 1). It is situated in the Sunda-Banda Arc which is host to numerous magmatic-hydrothermal deposits (Garwin et al., 2005), related to calc-alkaline magmatism resulting from subduction of the Indo-Australian Plate beneath the Eurasian plate. Prior to the start of open pit mining, Batu Hijau contained an estimated 1644 Mt of ore with copper and gold grades of 0.44% and 0.35 g/t respectively (Cooke et al., 2005).

The Batu Hijau district is largely made up of an Early to Middle Miocene volcaniclastic sequence which comprises volcanic lithic breccias and volcanic sandstones with local limestone layers. This is cut by several intrusive phases dating from the Early to Middle Miocene onwards which include andesites and andesite porphyries, quartz diorites, and porphyritic tonalites (Garwin, 2002). Mineralisation is strongly associated with tonalite porphyries in four main centres: Batu Hijau, Sekongkang, Arung Ara and Katala (Fig. 2). Batu Hijau is significantly larger and higher grade than the rest (Garwin, 2002). At least three intrusive episodes occurred in the Batu Hijau tonalite porphyry complex at the core of the system, with mineralisation and alteration intensity decreasing with each subsequent intrusion (Clode et al., 1999).

Potassic alteration, in the core of the Batu Hijau system, is typified by the replacement of hornblende groundmass in the host tonalites by biotite and magnetite. The surrounding propylitic alteration can be split into three subzones which, in order of increasing distance outwards, comprise: (1) actinolite \pm epidote \pm chlorite; (2) epidote + chlorite; and (3) chlorite (replacing mafic minerals) \pm calcite \pm albite (Fig. 2; Garwin, 2002; Clode et al., 1999). A transitional chlorite-sericite (intermediate argillic zone) developed after the propylitic and potassic alteration stages, overprinting the biotite (potassic) and actinolite zones (Idrus et al., 2009). Late-stage, structurally-controlled, argillic and advanced argillic alteration are widespread and overprint earlier alteration (Fig. 2; Clode et al., 1999; Garwin, 2002; Idrus et al., 2009).

3. Methodology

Short-wave infrared (SWIR) spectra were collected for 90 samples from the Batu Hijau deposit (Table 2). Samples were scanned in dark laboratory conditions using an ASD TerraSpec 4 reflectance spectrometer with the Hi-Brite Contact Probe accessory that acts as an illumination source and collects reflected light. Technical specifications are outlined in Table 1. Samples consisted of resin-mounted, polished rock slices, providing an ideal flat surface for the contact probe. Spectral files were created as an average of 3 scans at different points on each sample. Double the recommended scan time was used (10 s, following the recommendation of Chang and Yang, 2012 for dark, low reflectance rocks) to increase signal-to-noise ratios. Two sets of spectral files were generated via this process for each sample, acquired on different days, to assess the impact of differences in ambient lighting. In general, there is excellent agreement between the replicates (Table 2).

Spectra were primarily analysed using *The Spectral Geologist* (TSG) software, and selected for further investigation based on classification and mineral identification by *The Spectral Assistant* (TSA), a matching algorithm which identifies a linear mixture of two minerals in the library that best match the spectrum (CSIRO, 2010). Only spectra determined to contain either chlorite or epidote as the principal SWIRactive mineral phase (Table 2) were used in the subsequent analysis.

 $\begin{tabular}{ll} $\mathsf{Table 2} \\ \mathsf{Summary of sample data and principal minerals identified in SWIR spectra. \\ \end{tabular}$

Halo secondary Chlorite or mineral epidote?	ite Chlorite iculite Chlorite lite Chlorite	llite Chlorite	nsite Chlorite te Chlorite		zoisite Other/Null Ilite Other/Null		zoisite Epidote		nitePX Epidote		Palygorskite Chlorite	te Other/Null		Aragonite Other/Null		ite	atch Other/Null	zoisite Other/Null	te Other/Null	nite		Rectorite Chlorite				FeMgChlorite Other/Null	zoisite Other/Null		rte Other/Null	tral Other/Null	lite Other/Null	
Halo primary Halo sec mineral mineral	FeMgChlorite Mg-illite Clinozoisite Vermiculite FeMgChlorite Mg-illite	FeMgChlorite Beidellite	FeMgChlorite Corrensite FeMgChlorite Epidote		Hornblende Clinozoisite Hornblende Beidellite	9	Vermiculite Clinozoisite		Epidote KaolinitePX	e	FeMgChlorite Palygo	Heulandite Epidote	,	Philipsite-Ca Aragonite			Vermiculite No match	Vermiculite Clinozoisite	Heulandite Epidote	te		FeMgChlorite Rectorite				Phillipsite-Ca FeMgC	Vermiculite Clinozoisite		Heulandite Epidote	Heulandite Aspectral	Beidellite Mg-illite	
al TSA secondary mineral (B) ^b	Epidote Epidote Epidote	Kaolinite-PX	Epidote Epidote	Ankerite	Epidote NULL	NULL	NULL		Kaolinite-PX	NULL	Epidote	Muscovite		NULL	Epidote	Epidote	NULL	Muscovite	Epidote	Zoisite	NULL	Paragonite	Epidote	NOIT		NOLL	NULL	NULL	NOLL	NULL	NULL	
TSA primary mineral	Chlorite-FeMg Chlorite-FeMg Chlorite-FeMg	Chlorite-FeMg	Chlorite-FeMg Chlorite-FeMg	Chlorite-FeMg	Hornblende NULL	NULL	Epidote	;	Epidote Muscoxiite	NULL	Chlorite-Mg	Ankerite		Aspectral	Chlorite-FeMg	Muscovite	NULL	Siderite	Muscovite	Chlorite-FeMg	NULL	Chlorite-FeMg	Chlorite-Mg	Aspectral		Aspectral	NOLL	NULL	Aspectral	Aspectral	Paragonite	
TSA secondary mineral (A) ^b	Epidote Epidote Epidote	NOLL	Epidote Epidote	NULL	Epidote NULL	NULL	Paragonite	;	Kaolinite-PX	NULL	Epidote	Muscovite	;	NULL	Ankerite	Epidote	NOLL	Kaolinite-PX	Ankerite	NULL	NOIL	Paragonite	Epidote	NOLL	;	NOLL	NULL	NULL	NOLL	NOLL	Ankerite	
TSA primary mineral (A) ^b	Chlorite-FeMg Chlorite-FeMg Chlorite-FeMg	Chlorite-FeMg			Homblende NULL	NOLL	Ankerite	;	Epidote		Chlorite-Mg	Ankerite		Aspectral			NULL	Ankerite	Muscovite			Chlorite-FeMg				Aspectral			Aspectral	Aspectral	Paragonite	
Rock type	Andesite Andesite porphyry Volcanic	Volcanic	sandstone Andesite porphyry Andesite porphyry	Volcanic lithic breccia	Andesite porphyry Volcanic lithic	breccia Volcanic lithic	breccia Volcanic lithic	breccia	Andecite nornhymy	Andesite porphyry	Volcanic lithic	breccia Volcanic lithic	breccia	Andesite porphyry	Andesite porphyry	Andesite porphyry	Volcanic lithic	breccia Volcanic lithic	breccia Andesite porphyry	Andesite porphyry	Andesite porphyry	Andesite porphyry	Andesite porphyry	Volcanic lithic	breccia	Volcanic lithic breccia	Andesite porphyry	Andesite porphyry	Volcanic lithic breccia	Volcanic lithic	breccia Volcanic lithic	breccia
Lateral distance to centre (m)	2615 2611 2607	2783	2982 2297	1993	1931 1873	1451	1211		3636	1924	2000	2048		2293	2608	2356	2080	1928	1736	1367	1218	934	643	2576	,	2610	2699	2972	3173	3380	3535	
UTM Northing	9007990 9007982 9007975	9008262	9008864	0006006	9009248 9009356	9009242	9009320		9008140	9008004	0262006	9007930		9007694	9008240	9008695	9008955	9009100	9009290	9000665	9009830	9010115	9010213	9007524		9007538	9007490	9007308	900/131	9889006	9006784	
UTM Easting	483270 483279 483287	482933	482597 483322	483645	483738 483817	484282	484605		483175	484293	484228	484207		484108	479680	479560	479425	479325	479230	479300	479335	479390	479410	483820		483754	483644	483374	483232	483163	483009	
Sample ID	B2-0.3 ^a B2-11.9 ^a B2-23.0 ^a	B3-3.2ª	BH-19 BH-20	BH-21	BH-22 BH-23	BH-24	BH-25		BH-57 BH04.45	BH04-52	BH04-53	BH04-54		BH04-55B	BH05-71 ^d	BH05-72 ^d	BH05-73 ^d	BH05-74 ^d	BH05-75 ^d	BH05-76 ^d	BH05-77	BH05-78	BH05-80 ^d	BH10-101		BH10-102	BH10-103	BH10-104	BH10-105	BH10-106	BH10-107	

(continued on next page)

I able 2 (continued)	nea)										
Sample ID	UTM Easting	UTM Northing	Lateral distance to centre (m)	Rock type	TSA primary mineral (A) ^b	TSA secondary mineral (A) ^b	TSA primary mineral (B) ^b	TSA secondary mineral (B) ^b	Halo primary mineral	Halo secondary mineral	Chlorite or epidote? ^c
BH10-109	482753	9006444	3930	Volcanic lithic	NULL	NULL	Aspectral	NULL	Laumontite	Vermiculite	Other/Null
BH10-110	482604	9006283	4130	Volcanic lithic	Aspectral	NULL	Aspectral	NULL	Heulandite	Vermiculite	Other/Null
				breccia					:		
BH10-111	482477	9006087	4344	Andesite porphyry	NULL According	NULL	Aspectral	NOLL	Phillipsite-Ca	Aspectral	Other/Null
BH10-112	482381	9005936	4510 4536	Andesite porpnyry	Aspectral	NOLL	Aspectral	NOLL	Hematite	Phillipsite-Ca Montmorillonite	Other/Null
611-01117	00000	170000	900	breccia	2000	2019110	Oracino	20000	A CHILLICATION		Ouici/ ivuii
BH10-114	482191	9005855	4692	Volcanic lithic	NULL	NULL	NULL	NULL	Laumontite	Aspectral	Other/Null
BH10 11E	401003	0006770	48.75	breccia	11110	IIIIN	MINI	I IIIN	Amongo		O+bo= /N:-11
Fn-01	481993	9002778	1425	Andesite porpnyry Volcanic lithic	Fnidote	NOLL	Fnidote	NOLL Prehnite	Aspectrai	Biotite	Cuner/ Inum Enidote
The de	00000	601000	071	breccia	rbinoic		Thrace		Throng		and a
Ep-02	485914	9007647	1579	Volcanic lithic	Chlorite-FeMg	ParagoniticIllite	Chlorite-FeMg	ParagoniticIllite	FeMgChlorite	Rectorite	Chlorite
Fn-03	485900	9007545	1663	Andesite nornhyry	Chlorite FeMa	Muscoxite	Chlorita-FaMa	Muscoxite	Stilmomelane	Clinozoisite	Chlorite
Ep-03	485898	9007343	1757	Andesite porpuyry	Aspectral	MIII I	Aspectral	MITT	Dhillinsite-Ca	Clinozoisite	Orber/Null
Ep-05	485883	9007322	1858	Volcanic lithic	Chlorite-FeMg	Paragonite	Chlorite-FeMg	Paragonite	Stilpnomelane	Clinozoisite	Chlorite
Ep-06	486130	9802006	2133	breccia Volcanic lithic	Epidote	NULL	Epidote	NULL	Epidote	Palygorskite	Epidote
•				breccia	•		•		•		•
Ep-07	485919	9006964	2311	Volcanic lithic	NULL	NULL	Aspectral	NULL	Phillipsite-Ca	Epidote	Other/Null
Ep-08	485751	9006859	2266	Andesite porphyry	NULL	NULL	NULL	NOLL	Stilpnomelane	FeMgChlorite	Other/Null
Ep-09	485011	9011502	2644	Diorite	Chlorite-FeMg	Paragonite	Epidote	Paragonite	Stilpnomelane	Epidote	Chlorite/
Ep-10	485007	9011760	2890	Volcanic lithic	NOIT	NOIT	NULL	NULL	Heulandite	Epidote	Epidote Other/Null
En-11	484951	9012003	3132	breccia Volcanic lithic	Aspectral	NIIII	Asnectral	NIIII	Phillinsite-Ca	Enidote	Other/Null
i				breccia			man der				
Ep-12	485333	9009875	1133	Andesite porphyry	Chlorite-FeMg	Paragonite	Chlorite-FeMg	Paragonite	Rectorite	FeMgChlorite	Chlorite
Ep-18	485875	9008347	1028 450	Andesite porphyry	NULL Chlorite Ma	NULL ParagoniticIllita	NULL Chlorita-Ma	NULL Paragoniti ellite	Vermiculite Montmorillonite	Epidote Fridote	Other/Null
496.6			2		91112112	, mag 0, min 1	91112112	200000000000000000000000000000000000000		- Prince	
SBD018-619	485615	9009112	373	Tonalite	Chlorite-Mg	ParagoniticIllite	Epidote	NULL	Stilpnomelane	FeMgChlorite	Chlorite/ Fridote
SBD021-	485633	9009146	465	Tonalite	PhengiticIllite	Chlorite-FeMg	Chlorite-FeMg	ParagoniticIllite	Mg-illite	FeMgChlorite	Chlorite
522.8 SBD130-21	484960	0098006	1134	Volcanic lithic	NULL	NULL	NULL	NULL	Corrensite	FeMgChlorite	Other/Null
SBD143-41	484715	9008462	1331	Volcanic lithic	Epidote	Paragonite	Chlorite-FeMg	Epidote	Epidote	Beidellite	Chlorite/
SBD143-49	484715	9008462	1326	breccia Volcanic lithic	Chlorite-FeMg	Paragonite	Epidote	Paragonite	FeMgChlorite	Rectorite	Epidote Chlorite/
				breccia	0	β		6	0		Epidote
SBD145-33	484841	9008488	1243	Volcanic lithic	Epidote	NULL	Chlorite-FeMg	Epidote	Stilpnomelane	Epidote	Chlorite/ Fpidote
SBD145-	484841	9008488	1214	Volcanic lithic	Chlorite-FeMg	Epidote	Chlorite-FeMg	Epidote	Epidote	FeMgChlorite	Chlorite
73.2 SBD145-83	484841	9008488	1206	Dreccia Volcanic lithic	Epidote	NOLL	Epidote	Calcite	Epidote	Clinozoisite	Epidote
SBD256-813	485607	9009204	236	Dreccia Tonalite	Chlorite-Mg	Epidote	Chlorite-Mg	Epidote	Stilpnomelane	FeMgChlorite	Chlorite
SBD257- 0965.6	485633	9008893	208	Tonalite	Chlorite-FeMg	Paragonite	Paragonite	Chlorite-FeMg	Stilpnomelane	Rectorite	Chlorite
										100)	(continued on next nage)

Table 2 (continued)

Sample ID	UTM Easting	UTM Northing	Lateral distance to centre (m)	Rock type	TSA primary mineral (A) ^b	TSA secondary mineral (A) ^b	TSA primary mineral (B) ^b	TSA secondary mineral (B) ^b	Halo primary mineral	Halo secondary mineral	Chlorite or epidote? ^c
SBD276- 876.4	485628	9009275	305	Carbonate	Kaolinite-PX	Paragonite	Kaolinite-PX	NULL	Jarosite	Phillipsite-Ca	Other/Null
SBD276- 912.6	485629	9009258	296	Ash Tuff	Epidote	Kaolinite-PX	Montmorillonite	Epidote	Stilpnomelane	Epidote	Epidote
SBD284-100	484945	9008575	1080	Andesite porphyry	Chlorite-Mg	Epidote	Chlorite-Mg	Epidote	FeMgChlorite	Palygorskite	Chlorite
35D 204- 1145	403413	9000924	120	ronante	GIIOI IIE-IMB	rinogopite	CIIIOI IIE-1418	raragonnucinne	Aeminemine	ышелине	CILIOTILE
SBD284-	484911	9008549	1161	Volcanic lithic	Epidote	NULL	Phlogopite	Epidote	Epidote	Montmorillonite	Chlorite/ Fnidote
SBD284-170 SBD284-	484973 484975	9008596	1011 1006	Andesite porphyry Andesite porphyry	Chlorite-Mg NULL	Epidote NULL	Chlorite-FeMg Chlorite-Mg	Epidote Epidote	FeMgChlorite Vermiculite	Montmorillonite Clinozoisite	Chlorite Other/Null
173.8 SBD284-20	484912	9008549	1160	Volcanic lithic	Epidote	NULL	NULL	NULL	Vermiculite	Clinozoisite	Epidote
SBD284-226	484995	9008614	957	breccia Volcanic lithic	NULL	NULL	Epidote	NULL	Vermiculite	Aragonite	Other/Null
SBD284-233	484998	9008616	950	Volcanic lithic	Epidote	NULL	NULL	NULL	Epidote	Palygorskite	Epidote
SBD284-266	485011	9008626	917	Volcanic lithic	NOLL	NULL	Epidote	NULL	Epidote	Palygorskite	Other/Null
SBD284-306	485027	9008638	879	Volcanic lithic	Hornblende	Ankerite	NULL	NULL	Vermiculite	Brucite	Other/Null
SBD284-375	485054	9008659	811	Volcanic lithic	Chlorite-FeMg	ParagoniticIllite	NULL	NULL	Beidellite	FeMgChlorite	Chlorite
SBD284-424	485073	9008675	764	Volcaniclastic	Chlorite-Mg	Muscovite	NULL Chlorita Ma	NULL	Vermiculite	Clinozoisite	Chlorite
SBD284-95	484943	9008573	1085	Andesite porphyry	NULL	NULL	NULL	NULL	Vermiculite	Aspectral	Other/Null
SBD284- 965.5	485323	0988006	247	Carbonate	NULL	NULL	Ankerite	Paragonite	Phillipsite-Ca	Paragonite	Other/Null
SBD284-97 SBD284-	484943 485404	9008574 9008916	1083	Andesite porphyry	Paragonite Chlorite-FeMg	Zoisite ParagoniticIllite	NULL	NULL	Clinoptilolite Stilpnomelane	Muscovite Vermiculite	Other/Null Chlorite
SBD284-840 SBD284-	485260 485323	9008815 9008860	363	Volcaniclastic	Chlorite-FeMg Homblende	ParagoniticIllite Paragonite	NULL	NULL	Stilpnomelane Vermiculite	FeMgChlorite Ammonio-Clay	Chlorite Other/Null
SBD299-	485540	9009360	404	Carbonate	Epidote	NULL	Epidote	NULL	Epidote	Palygorskite	Epidote
SBD304- 619.6	485621	9008676	374	Ash Tuff	Aspectral	NULL	Aspectral	NULL	Phillipsite-Ca	Hornblende	Other/Null

Sample data and classification of mineralogy determined from the spectra. Radial distances to the nearest major porphyry centre are given for each sample; this is to Batu Hijau for most of the samples, but to the Sekongkang system for samples in the western traverse. $^{\rm a}$ Samples collected from close to the Bambu epithermal vein system. $^{\rm a}$

^b (A) and (B) refer to the two separate sets of spectra acquired for each sample.

^c Principal mineral identified in spectra. "Chlorite/Epidote" refers to samples determined to be chlorite in one set of spectra and epidote in the other. It is probable that they contain roughly equal amounts of each.

^d Samples proximal to the Sekongkang porphyry centre (distances measured away from this).

 Table 3

 Summary of extracted spectral and compositional data.

Sample ID	2250	2340	1400	2250 nm	2340 nm	1400 nm	Hull slope	Data type		Chlorite data (EMP or LA-ICP-MS)	¶ or L	-ICP-MS				Epidote (EMP)	(EMP)	Whole rock
	nm λ position	nm λ position	nm λ position	depth	depth	depth	index ^c		Fe	Mg	Al 8	Si	Ca	Mg# /	Al/(Al	A	Fe	Mg#
	4		4												+Si)			
B2-0.3 ^a	2253.2	2339.7	1404.6	0.307	0.423	0.187	1.59	$\Gamma A^{\mathbf{p}}$	16.71	14.59	10.88		0.136 (0.466				0.37
B2-11.9 ^a	2254.2	2340.0	1407.2	0.357	0.501	0.085	1.36	LA	15.46		10.00	Ĭ	0.124 (0.405				0.29
$B2-23.0^{a}$	2254.2	2340.8	1407.3	0.178	0.298	0.132	1.59	ΓA	15.92	10.25	10.00	•	0.171 (0.392				0.28
B3-3.2ª	2254.4	2342.1	1406.6	0.256	0.313	0.347	2.04	LA			10.00	•	0.117 (0.397				0.26
BH-19	2253.1	2338.9	1404.6	0.187	0.279	0.231	1.21	ΓA^{b}	15.68	14.59	10.69	_	0.146 (0.482				0.31
BH-20	2253.4	2338.8	1402.4	0.134	0.282	0.127	1.34											0.32
BH-21	2252.0	2338.0	1400.8	0.414	0.502	0.398	1.96	ΓA^{b}	15.16		10.68	Ū		0.515				0.43
BH-22	2252.4	2330.5	1402.6	0.067	0.169	0.071	1.21	LA	15.59	16.06	10.04	•	0.026	0.507				0.33
BH-23	2250.2		1398.8		0.070	0.039	1.10											0.33
BH-24	2252.1	2335.6	1400.7	0.121	0.200	0.124	1.30	EMP	13.88						0.429			0.30
BH-25	2251.0	2339.0	1408.2	0.055	0.074	0.044	1.14	EMP	12.41	13.28	11.19	12.76 (0.100	0.517 (0.467			0.26
BH-57	2254.4	2339.7	1413.0	0.070	0.203	0.051	1.07											
BH04-45	2252.8	2338.7		0.076	0.118		1.21	ΓA	14.02		8.90							0.03
BH04-52	2248.4	2328.0	1401.9	0.025	0.037	0.027	1.05	EMP	13.41		8.83			_	0.382			0.29
BH04-53	2252.7	2341.3	1408.0	0.093	0.183	0.035	1.24	EMP	13.47		9.83				0.412			0.23
BH04-54	2252.1	2341.6	1414.7	0.028	0.078	0.054	1.16	EMP	12.86		10.49			0.458 (0.413			0.30
BH04-55B	2249.7	2342.6		0.011	0.009	0.046	1.07	EMP	12.13		9.31				0.384			0.34
BH05-70B	2252.0	2337.7	1400.1	0.093	0.139	0.085	1.18	EMP	13.31	12.86	9.52			0.491 (0.408	11.76	10.54	0.27
BH05-71	2252.5	2338.9	1404.4	0.086	0.127	0.075	1.14	EMP	11.35	14.11	10.06				0.424	11.93	10.11	0.27
BH05-72	2252.5	2340.9	1410.2	0.040	0.097	690.0	1.16	EMP	16.21		C				0.451	11.17	11.57	0.24
BH05-73	2251.6		1402.6	0.049	0.172	0.144	1.52	EMP	17.46						0.428	13.91	7.21	0.33
BH05-74	2249.8	2336.3	1407.2	0.030	0.046	0.056	1.08	EMP	12.16						0.400	11.83	9.81	0.31
BH05-75	2251.5	2342.1	1413.6	0.065	0.102	0.124	1.18	EMP	11.90		01				0.450			0.28
BH05-76	2252.9	2339.5	1401.6	0.086	0.117	0.100	1.27	EMP	16.13		6.38				0.409	12.78	8.35	0.30
BH05-77			1397.0	0.092	0.097	0.106	0.92	EMP	17.54						0.344			0.35
BH05-78	2251.8	2339.6	1403.3	0.235	0.279	0.337	1.33	EMP	14.14		<u>~</u>				0.449			0.48
BH05-79	2252.0	2336.9	1399.9	0.068	0.111	0.120	1.11	EMP	16.99						0.421	12.01	10.25	0.29
BH05-80	2252.3	2332.3	1401.9	0.071	0.149	0.124	1.15	EMP	14.55						0.439	11.93	10.39	0.32
BH10-101	2246.3	2338.9		0.013	0.009	0.062	1.06	EMP	12.54		_				0.422			0.31
BH10-102	2249.8	2339.6		0.016	0.018	0.056	1.06	EMP	13.29						0.387			0.31
BH10-103	2250.5	2327.0	1399.8	0.031	0.050	0.071	1.03	EMP	14.25						0.370	;	;	0.35
BH10-104	2249.5	2338.5	1414.6	,	0.012	0.056	1.02	EMP	29.6		~				0.404	11.07	10.83	0.27
BH10-105	2249.5	2334.8		0.016	0.022	090.0	1.08	EMP	11.80		9.47				0.384	11.90	10.19	0.32
BH10-106	2249.0	2328.6		0.008	0.010	0.059	1.10	EMP	11.55						0.383	11.84	9.98	0.32
BH10-107	2248.0	2340.4	1411.5		0.031	0.086	1.03	EMP	11.09	11.50	11.18	14.74	0.322	0.509	0.431			0.32
BH10-108	2243.2	2320.2		2000	0.012	600.0	1.00	FMD	12.10						0.5/5			0.24
DI110-109	2240.2	0.141.0		0.007	0.019		1.09	EME	12.30						0.00			0.29
BH10-111	2243.0	6.7262		0.003	0.013	2200	1.04	FMP	7.81						0.349			0.32
BH10-112	22.48.4				0.00	0.112	1.02	I.A	7.30						0.310			0.33
BH10-113	2250.5		1415.0		0.066	0.067	1.15	EMP	10.51		60.8				0.338			0.29
BH10-114	2243.2	2325.3			0.013		1.01	EMP	10.05		8.21				0.339			0.35
BH10-115	2251.3	2327.0	1409.4	0.044	0.037	0.090	1.01	LA	17.27		60.9				0.263			0.25
Ep-01	2252.4	2342.1	1402.8	0.180	0.434	0.040	1.13	EMP	14.88		10.36				0.449	13.22	8.19	0.27
Ep-02	2254.4	2342.6	1406.7	0.183	0.309	0.361	1.47	EMP	17.54		10.01			0.354 (0.448	11.71	10.95	0.29
Ep-03	2252.9	2343.3	1410.3	0.112	0.163	0.296	1.52	EMP	16.93	10.21					0.444	13.08	8.71	0.30
Ep-04	2248.9	2346.4	1414.3	0.026	0.070	0.121	1.13	EMP	18.43	9.32	9.64		0.194 (0.336 (0.417	11.51	10.73	0.24
Ep-05	2252.7	2342.3	1406.6	0.119	0.167	0.256	1.65	EMP	15.43	10.83	10.43	13.37	0.129 (0.412 (0.438			0.33
Ep-06	2252.8	2338.7	1411.0	0.122	0.329	0.035	1.20	EMP	13.09	11.85	10.57				0.444	13.19	8.22	0.30
Ep-07	2250.6	2338.0	1413.3	0.040	0.066	0.105	1.22	EMP	12.92	12.28	_		0.152 (0.420	12.16	9.41	0.33
Ep-08	2251.7	2331.1	1400.9	0.051	0.066	0.093	1.11	EMP	15.89		8.52	13.77 (0.427 (0.382			0.35
																	(contin	(continued on next page)

Table 3 (continued)

(namina) o arani																		
Sample ID	2250	2340	1400	2250 nm	2340 nm	1400 nm	Hull slope	Data type		data (I	Chlorite data (EMP or LA-ICP-MS)	\-ICP-M.	S)			Epidote (EMP)	(EMP)	Whole rock
	nm λ position	nm λ position	nm λ position	depth	depth	depth	index ^c		Fe	Mg	A	Si	Ca	Mg#	Al/(Al + Si)	W	Fe	Mg#
00	0.000	0000	1407	0	100.0	2100	L .	9	14.06	7.	10.40	2,0	0 1 7 7	77	7	11 40	5	00
Ep-09	7251.7	2339.0	1403.8	0.138	0.038	0.210	1.04	EMB	11.60	10.07	10.40	13.40	0.279	7447	0.439	11.40	10.70	0.30
Fh-11	2251.2	2339.0	7.01	0.024	0.030	0.067	1.08	FMP	12.32	19.53	10.00	13.82	0.163	0.504	0.420	12.03	9.87	0.33
Ep-12	2252.3	2341.2	1409.2	0.052	0.055	0.069	1.09	EMP	11.95	13.24	11.68	12.50	90000	0.526	0.483	i	2	0.21
Ep-18	2250.1	2331.7	1415.5	0.024	0.058	0.051	1.06	EMP	10.29	14.23	10.50	13.34	0.108	0.580	0.440	12.52	9.19	0.33
SBD018-496.6	2248.6	2337.8	1409.6	0.045	0.056	0.119	1.05	EMP	13.00	12.83	10.42	13.21	0.074	0.497	0.441	11.78	10.42	0.20
SBD018-619	2251.8	2337.6	1409.6	0.070	0.105	0.095	1.10	EMP	11.61	13.83	99.6	13.68	0.084	0.544	0.414			0.20
SBD021-522.8	2249.0	2338.9	1410.3	0.044	0.081	0.141	1.15	EMP	14.42	11.84	10.83	12.75	0.040	0.451	0.459	12.54	9.11	0.17
SBD130-21	2249.4	2326.2	1396.4	0.064	0.107	0.070	1.09	EMP	11.37	13.99	10.57	13.23	0.048	0.552	0.444			0.29
SBD143-41	2254.2	2340.9	1408.8	0.185	0.343	0.065	1.19	EMP	14.16	6.62	11.55	13.42	0.185	0.413	0.463			0.29
SBD143-49	2254.4	2340.9	1408.3	0.175	0.278	0.137	1.39	EMP	16.47	9.53	12.02	12.48	0.074	0.367	0.491			0.31
SBD145-33	2252.8	2339.4	1409.7	0.163	0.295	0.182	1.28	EMP	14.04	11.67	10.92	13.18	980.0	0.454	0.453			0.29
SBD145-73.2	2253.2	2338.4	1402.8	0.339	0.540	0.127	1.58	EMP	15.00	11.94	10.80	12.80	0.046	0.443	0.458			0.28
SBD145-83	2253.7	2339.0	1410.0	0.274	0.521	0.033	1.21	EMP	15.21	11.04	11.66	12.21	0.074	0.420	0.489			0.28
SBD256-813	2250.9	2335.7	1403.3	0.071	0.115	0.134	1.18	EMP	11.14	13.36	9.71	13.59	0.134	0.545	0.417	12.17	9.76	0.26
SBD257-	2251.8	2338.8	1409.7	0.089	0.164	0.268	1.28	EMP	13.08	12.68	10.44	13.00	0.064	0.492	0.445	11.46	11.31	0.17
0962.6																		
SBD276-876.4	2250.9	2332.3	1414.1		0.043	0.180	1.22									12.49	60.6	0.44
SBD276-912.6	2252.3	2336.8	1412.4	0.128	0.326	0.250	1.39									12.18	10.19	0.20
SBD284-100	2250.9	2338.3	1401.7	0.076	0.111	0.043	1.15	ΓA^{b}	13.28	17.14	10.00		0.029	0.563				0.34
SBD284-1145	2249.6	2329.1	1404.5	0.034	0.085	0.110	1.42	EMP	14.34	11.88	10.48	12.96	0.097	0.453	0.447			0.17
SBD284-17.5	2253.0	2339.7	1408.8	0.115	0.220	0.113	1.25	EMP	15.01	11.75	10.82	12.60	0.034	0.439	0.462			0.28
SBD284-170	2250.3	2336.5	1402.9	0.077	0.100	0.042	1.17	EMP	11.12	14.42	10.59	13.23	0.027	0.565	0.444			0.31
SBD284-175.8	2248.1	2325.2	1400.2	0.029	0.049	0.040	1.07	EMP	10.78	14.56	10.67	13.35	0.086	0.574	0.444			0.31
SBD284-20	2252.2	2339.6	1408.6	0.104	0.164	0.108	1.31	EMP	14.46	12.27	10.96	12.73	0.029	0.459	0.463			0.26
SBD284-226	2250.2		1396.0		0.052	0.046	1.04	EMP	10.21	14.63	10.70	13.76	0.127	0.589	0.437			0.31
SBD284-233	2253.2	2338.1		0.113	0.365	0.032	1.12	EMP	16.07	9.47	9.91	14.32	0.469	0.371	0.409			0.14
SBD284-266	2253.9	2339.7	1419.9	0.063	0.214	0.017	1.03	EMP	11.84	14.42	10.32	13.53	0.038	0.549	0.433			0.27
SBD284-306	2248.1		1399.0	0.010	0.028	0.028	1.02	EMP	10.90	14.45	10.59	13.45	0.040	0.570	0.440			0.29
SBD284-375	2251.3	2340.1	1412.5	0.041	0.062	0.090	1.05	EMP	11.84	13.03	11.57	13.15	0.028	0.524	0.468			
SBD284-424	2249.4	2334.1	1401.1	0.053	0.065	0.042	1.14	EMP	11.75	13.65	9.16	14.49	0.163	0.537	0.387			0.25
SBD284-775		2347.0	1417.4		0.014	0.165	1.45											0.18
SBD284-95	2250.0	2330.2	1402.8	0.055	0.070	0.074	1.20	EMP	11.61	13.90	10.88		0.034	0.545	0.459			0.33
SBD284-965.5	2251.7	2339.9	1413.9	0.025	0.051	0.074	1.23	EMP	12.16	12.98	10.85		0.075	0.516	0.453			0.25
SBD284-97	2249.9	2339.7	1413.7		0.038	0.108	1.18	EMP	11.94	13.60	10.88	12.96	0.039	0.532	0.456			0.25
SBD284-1124	2250.8	2333.9	1411.7	0.036	0.060	0.074	1.35											
SBD284-840	2251.8	2336.5	1408.7	0.080	0.122	0.095	1.40											0.38
SBD284-965.6	2253.0	2343.5	1412.2		0.071	0.157	1.23											
SBD299-	2252.8	2336.5	1414.1	0.143	0.417	0.120	1.32									11.22	11.55	0.13
0772.5		,					,									:		
SBD304-619.6	2251.1	2331.0		0.021	0.094	0.170	1.16	EMP	19.76	9.11	10.48	12.19	0.075	0.315	0.462	11.41	11.54	0.17

All geochemical data (except ratios) reported in weight percent, and averaged from multiple readings per sample. Outliers were removed prior to averaging (see text for details). Geochemical data are derived from the AMIRA P765A project

 $^{\rm a}$ Samples collected from close to the Bambu epithermal vein system. $^{\rm b}$ LA-ICP-MS data with anomalously elevated Fe and Mg values (not used in analysis). $^{\rm c}$ 'Hull slope index' = reflectance at 1850 nm/reflectance at 1440 nm.

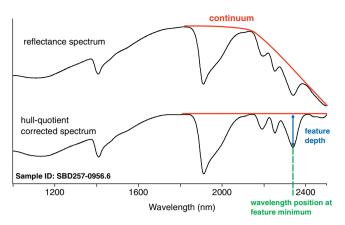
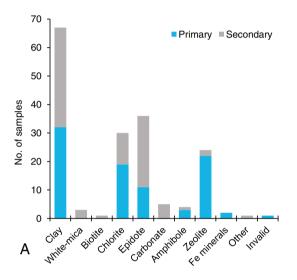


Fig. 3. A standard reflectance spectrum (top) compared to a spectrum with the hullquotient correction applied (bottom) which removes the continuum caused by broader background variation. The feature depth and the wavelength position at minimum, two important spectral characteristics, are also illustrated for one absorption feature.



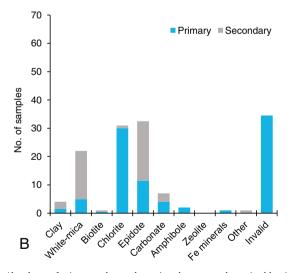


Fig. 4. Abundance of primary and secondary mineral groups as determined by: (A) *The Spectral Assistant* (TSA); and (B) the Halo mineral identifier. Invalid refers to samples where no mineral could be identified from the spectrum.

Wavelength positions and depths of features were calculated from the two average spectra for each individual sample. The average of these results are given in Table 3. These values were extracted from the profiles of hull-quotient corrected spectra; this correction accentuates absorption features by removing broad background variation (Fig. 3).

Analysis of the spectra was also undertaken by ASD Inc. (PANalytical) utilising the Halo mineral identifier in order to compare results obtained using a different matching algorithm. The considerably larger library of mineral spectra that Halo incorporates also enabled the identification of additional minerals that TSG could not.

Geochemical data were previously collected as part of the AMIRA P765A project. These data include whole-rock geochemistry, electron microprobe analyses (EMP) of chlorite and epidote grains, and laser ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS) analyses of chlorite grains (Table 3). EMP data were primarily used to define the major element compositions of minerals; this was acquired on multiple spots on multiple grains in each sample, with an average of 10 measurements per sample. These were validated based on stoichiometry prior to inclusion in the database. Chlorite LA-ICP-MS data were used to define major element chemistry in four samples where EMP data were not available. Outliers in the EMP data were identified as any measurements where at least one major element (Fe, Al, Si, O, Mg, Ca) fell outside the bounds of the mean of the dataset $\pm 2\sigma$ for each mineral. Multiple spot analyses for each sample were averaged and \pm 1σ standard error used as a practical measure of combined analytical uncertainty and natural, within-sample variability.

4. Results

4.1. Spectrally-determined mineralogy

The Spectral Assistant identified chlorite and epidote as the most abundant SWIR-active mineral groups in the samples, with white-mica and carbonates also making up significant contributions (Figs. 4A, 5A, B). Chlorite, where identified, was almost always the primary mineral. Epidote was common as the second most abundant SWIR-active mineral in chlorite-domincary mineral. The results from Halo (Figs. 4B, 5B) were generally similar, but identified clays (primarily smectites and vermiculites) as dominant in the biotite and actinolite zones, with chlorite commonly attributed as the secondary mineral. Although the identification of these phases should be treated with caution, their presence would be consistent with the later argillic overprint that has been well mapped in the proximal parts of the alteration system (Fig. 2). Halo also classified many spectra that TSA could not, with most being zeolite-dominant, particularly in the very distal samples. Minerals contained in each group are shown in Table 4.

Of the 90 samples, 46 produced spectra with the primary mineral identified by TSA as either chlorite or epidote (Fig. 5C). Of this subset, 30 were attributed to containing primarily chlorite, 10 to containing primarily epidote, and 6 where it was unclear (likely containing roughly equal amounts of each). Separate spectra collected on different areas of the same sample were very consistent (Fig. 6) indicating that the SWIR response is reproducible and varies more between samples (as a function of spatial position and mineral abundance) than within samples.

4.2. Chlorite

Chlorite chemistry from throughout the propylitic zones at Batu Hijau shows significant variation in terms of Fe and Mg which have a strong inverse correlation (Fig. 7A) related to the well-established solid solution between the iron and magnesium end-members (Deer et al., 2009). The Mg/(Mg + Fe) mass ratio (Mg#) ranges from 0.30 to 0.62 which translates to Mg/Fe molar ratios between 0.78 and 0.51 with a mean of 0.68 \pm 0.01 (1 σ). Comparison of chlorite Mg# to the wholerock Mg# shows no correlation (Fig. 7B) suggesting a lack of protolith control of chlorite composition. Si content shows an inverse correlation with Al (Fig. 7C), probably as a result of the Tschermak substitution: $Al^{3+} + Al^{3+} = Si^{4+} + M^{2+}$ (Deer et al., 2009). Ca is also strongly

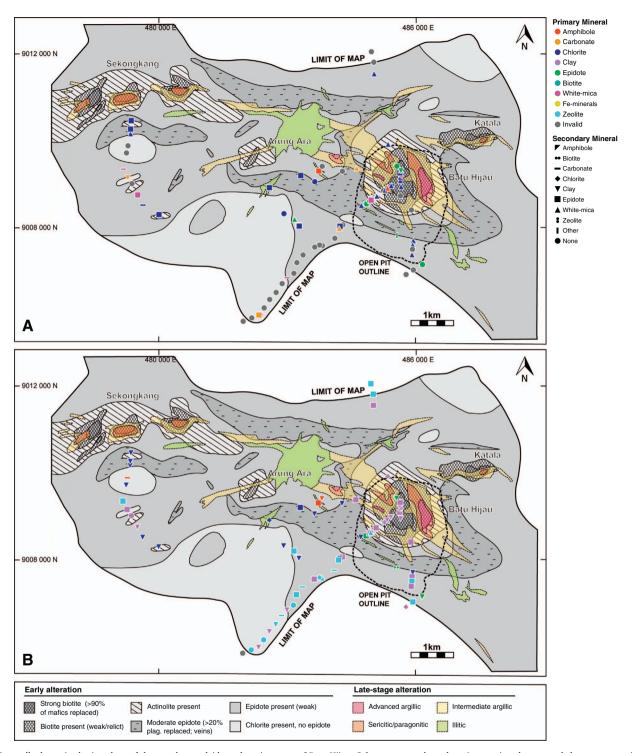


Fig. 5. Spectrally-determined mineralogy of the samples overlaid on alteration maps of Batu Hijau. Colour corresponds to the primary mineral group and shape corresponds to the secondary mineral group. (A) Classification of spectra by *The Spectral Assistant*. (B) Classification of spectra as determined by The *Halo* mineral identifier. (C) Samples classified according to their dominant mineral (from TSG). 'Chlorite/Epidote' refers to samples classified as chlorite in one instance, and epidote in the other – it is probable that they contain roughly equal amounts of each. Samples classified as 'Other/Invalid' were not used in any analysis involving spectral features. Base map modified after Garwin (2000).

correlated with Si and inversely correlated with Al (Fig. 7D).

Chlorite-dominated spectra are characterised by two key absorption features centred around 2250 nm and 2340 nm (Fig. 8), caused by Fe–OH and Mg–OH bond stretching respectively (Herrmann et al., 2001). A third feature occurs at around 2000 nm but this is masked by a large feature at 1910 nm, present in all samples, that is attributable to the presence of molecular water. A feature at around 1400 nm is also

consistently present, caused by OH $^-$ (Clark et al., 1990; Bishop et al., 2008), but is not diagnostic of chlorite. In many samples, an absorption feature at around 2195 nm is probably a result of the presence of clay minerals containing Al-OH groups (Clark et al., 1990; Herrmann et al., 2001). There is also a notable slope (hull) that descends from $\sim\!1900$ nm to $\sim\!1400$ nm with variable gradient.

Within the spectra classified as chlorite-dominant, the most

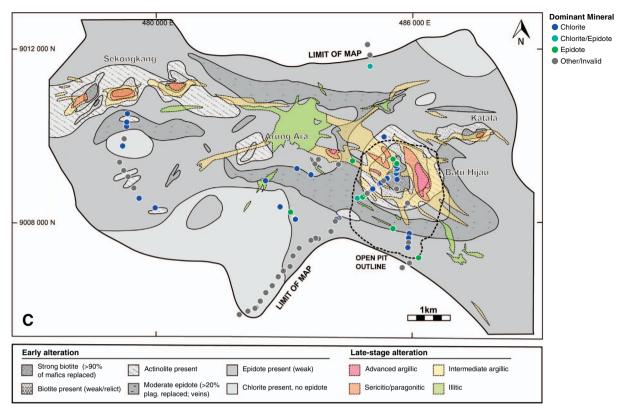


Fig. 5. (continued)

Table 4 Classification of minerals (as identified and named by TSG and Halo) into mineral groups used in Figs. 4, 5A, 5B.

Amphibole	Biotite	Carbonate	Chlorite	Clay	Epidote	Fe-minerals	White-mica	Zeolite	Other
Hornblende	Biotite Phlogopite	Calcite Aragonite Dolomite Ankerite Siderite	Chlorite Corrensite	Mg-illite Vermiculite Beidellite Palygorskite Kaolinite Montmorillonite Iron saponite Rectorite Ammonio-clay Stilpnomelane	Epidote Clinozoisite Zoisite	Hematite Jarosite	Muscovite Paragonite Paragonitic illite Phengitic illite	Chabazite Heulandite Philippsite-Ca Harmotome Laumontite Clinoptilite	Brucite Prehnite

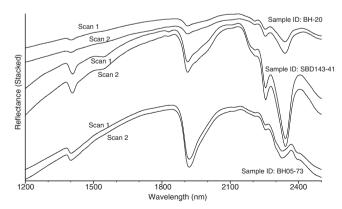


Fig. 6. Comparisons between two, separately obtained spectra taken for the same sample (shown in three examples). Spectra are very consistent despite being obtained separately on different days, at different points on each rock sample.

noticeable variation occurs in the position and depth of absorption features centred around 2250 nm and 2340 nm, which are strongly coupled (Fig. 9). For the absorption centred around 2250 nm, the exact wavelength position of the feature minimum varies between 2255 nm and 2248 nm. For the absorption centred around 2340 nm this varies between 2343 nm and 2328 nm. The maximum depth of both features varies between 0.03 and 0.55 (fraction of reflectance range).

The positions of these two features show a relatively strong inverse correlation with the Mg# of chlorite in the samples (Fig. 10). Samples containing more Mg-rich chlorite correspond to spectra where both the 2250 nm and 2340 nm features are shifted to lower wavelengths. Spectra with absorption feature minima at the lowest wavelengths appear to be anomalous, with wavelength values more in fitting with the samples not classified as chlorite-dominated.

The depth of both features also shows a negative correlation with the Mg#, which is considerably stronger at depths below ~ 0.34 (Fig. 11). Data points with greater depth values appear to be more in the range of depths shown by epidote-dominated samples.

Changes in the slope of the hull between 1900 nm and 1400 nm are $\,$

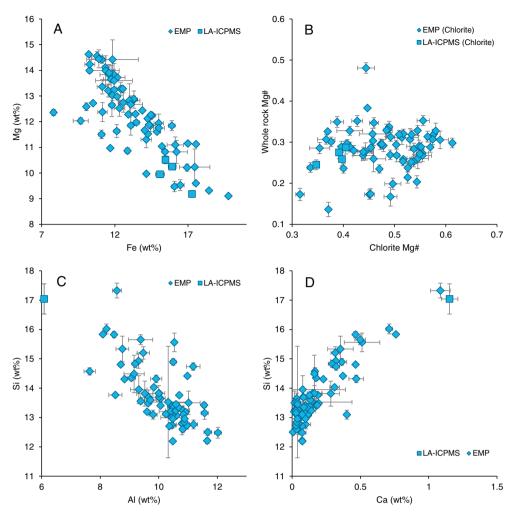


Fig. 7. Plots of element concentrations for chlorite grains. Data are averaged for each sample and 1σ standard error bars are shown. EMP and LA-ICPMS data are shown in different symbols. (A) Mg concentration plotted against Fe concentration showing a positive correlation. (B) Whole rock Mg# plotted against chlorite Mg# showing no correlation (R² = 0.017). Si concentration plotted against Al concentration for chlorite grains. A negative correlation is seen between Si and Al content. (D) Si concentration plotted against Ca concentration showing a positive correlation. Data derived from AMIRA P765A project database.

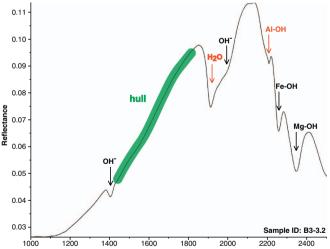


Fig. 8. SWIR spectrum of a sample predominantly made up of chlorite (according to *The Spectral Assistant*). Diagnostic features include the Fe-OH and Mg-OH absorption features at $\sim\!2250$ and $\sim\!2340$ nm, the weak (masked) feature at $\sim\!2000$ nm and the hull between $\sim\!1900$ nm and $\sim\!1400$ nm. Red labels indicate features in the spectrum caused by the presence of other minerals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

also observed, with more Fe-rich samples having a steeper slope (Fig. 12). The aforementioned features are illustrated in selected spectra (Fig. 13).

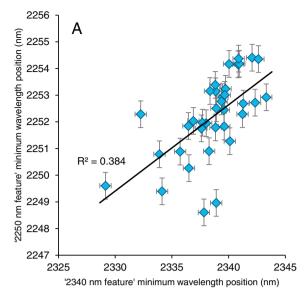
The position of the OH^- absorption feature at around 1400 nm also shows systematic variation which correlates fairly strongly with the Al:Si ratio of chlorite in the samples, with Al-rich chlorite producing spectra with the feature shifted to higher wavelengths (Fig. 14).

4.3. Epidote

Epidote geochemistry shows most variation with respect to Fe and Al (Table 3) representing the solid solution between epidote and clinozoisite. Molar Fe:Al ratios range from 0.50 to 0.24, meaning all samples (except one) fall into the classification of epidote (Franz and Liebscher, 2004). Other major elements, including Ca, show remarkably little variation.

In epidote-dominated spectra (Fig. 15) two absorptions are once again observed at around 2250 nm and 2340 nm, caused by Fe–OH bonds (Clark et al., 1990). However, the most diagnostic feature occurs at \sim 1550 nm and the presence of epidote in a sample is most readily identified by this. Once again, absorptions are seen at \sim 1400 nm and \sim 1910 nm.

The range in wavelength positions of the 2250 nm and 2340 nm absorption features (2251-2255 nm and 2336-2342 nm respectively) is significantly less than in chlorite. The depth of the 2340 nm feature is generally greater than in chlorite (mean = 0.3 compared with 0.2) but that of the 2250 nm absorption is about the same (Table 3). No significant variations in absorption features were observed that correlate with chemical composition (e.g. the Fe:Al ratio), however this may be due, in part, to a paucity of data.



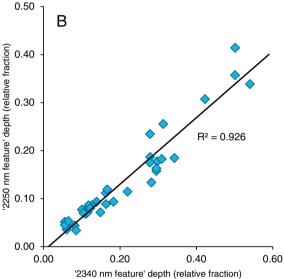


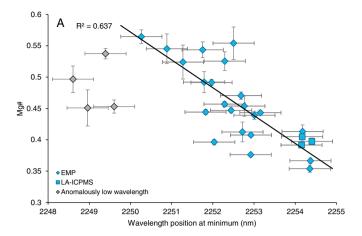
Fig. 9. Plots showing the coupling of absorption features at 2250 nm and 2340 nm. (A) Wavelength positions at absorption minima showing a positive correlation. (B) Relative absorption depths showing a positive correlation.

4.4. Spatial patterns in chlorite spectral response and chemistry

A number of spectral and chemical features of chlorite vary spatially, relating primarily to distance away from the Batu Hijau porphyry centre and from the Sekongkang prospect.

4.4.1. 2250 and 2340 absorption positions

The wavelength position of the features at 2250 nm and 2340 nm are lowest near the centre of the Batu Hijau system, and show a systematic shift to longer wavelengths away from the centre, providing a strong vector to the orebody (Fig. 16). Plotting the data as a function of radial distance from the centre reveals a general increase of the wavelength positions from the centre to ~ 1.2 km, beyond which the values generally plateau (Fig. 17), approximately coincident with the edge of the actinolite subzone. The 2340 nm feature also follows this trend in the northwest with respect to the Sekongkang porphyry centre (Fig. 16B).



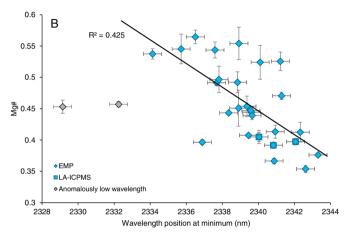


Fig. 10. Chlorite Mg# plotted against the wavelength position at absorption feature minimum for: (A) the 2250 nm absorption; and (B) the 2340 nm absorption. Both features show a reasonably strong negative correlation. Outliers are present at lower wavelengths (shown in grey). Linear regression lines are shown (excluding outliers). Vertical error bars are 1σ standard error (propagated through the ratio calculation). Horizontal error bars are \pm 0.5 nm representing the measurement precision of the spectrometer.

4.4.2. 2250 and 2340 absorption depths

The depths of the 2250 nm and 2340 nm absorptions show similar patterns, deepening systematically away from the porphyry centre (Fig. 18). The vector to mineralisation remains strong, albeit less clear than in the case of wavelength positions. The Sekongkang prospect is not picked out by feature depth variation which is interesting as a potential discriminator between well-mineralised and poorly mineralised systems. Unlike the wavelength positions, absorption depths continually deepen away from the centre (Fig. 19), although values are unusually elevated at around 1 km to 1.5 km.

4.4.3. Major element chemistry

The chlorite Mg/Fe substitution, as reflected by the Mg#, is likely to be the principal control on absorption position and possibly depth. This also shows systematic, but slightly more complicated, changes from the centre outwards (Fig. 20). Chlorite, within approximately 1 km of the centre, is enriched in Mg and then shows a rapid decrease in Mg:Fe ratio to around 1.5 km; beyond this, the relative content of Mg increases progressively to the limit of sampling at about 4.5 km. Samples at distances less than 500 m from the centre (which correspond to tonalite and carbonate-hosted chlorite) are anomalous, as previously identified in chlorite trace element chemistry (Wilkinson et al., 2015).

The Al:Si ratio in chlorite shows a fairly strong inverse correlation with distance, particularly at distances beyond 3 km from the centre (Fig. 21). However, this is not reflected in any obvious spatial variation

0.35

0

0.1

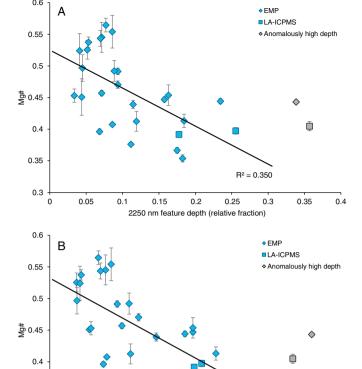


Fig. 11. Chlorite Mg# plotted against the relative depth of absorption features for: (A) the 2250 nm absorption; and (B) the 2340 nm absorption. Both features show a negative correlation. Depths greater than \sim 0.34 are thought to be outliers possibly due to epidote in the sample (shown in grey). Vertical error bars are 1 σ standard error (propagated through the ratio calculation). Horizontal error bars calculated from the signal-to-noise ratio of the spectrometer are not shown as they were determined to be negligible (\pm 0.025%).

0.2

0.3

2340 nm feature depth (relative fraction)

 $R^2 = 0.406$

0.4

0.5

0.6

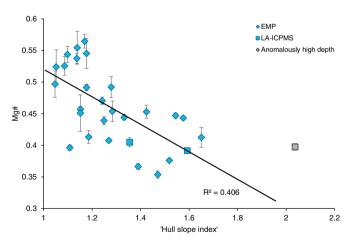


Fig. 12. Chlorite Mg# plotted against the 'hull slope index' (reflectance at 1850 nm/ reflectance at 1440 nm) which corresponds to the slope of the hull. Greater values represent steeper slopes. Data points at the highest end appear anomalous (shown in grey) and may reflect the presence of other Fe-bearing minerals in the samples. Vertical error bars are 1σ standard error (propagated through the ratio calculation). Horizontal error bars calculated from the signal-to-noise ratio of the spectrometer and error propagation are not shown as they were determined to be negligible (\pm 0.06% and lower).

in the position of the 1400 nm feature (which is thought to be correlated with Al/[Al + Si]). This may be due, in part, to that fact that no samples beyond 3 km displayed chlorite-dominated spectra.

5. Discussion

The results from this study support the effectiveness of reflectance spectroscopy in discriminating alteration zones (e.g. Sun et al., 2001; Jones et al., 2005; Zadeh et al., 2014). In detail, the minerals identified in spectra are generally consistent with the documented alteration mineralogy around Batu Hijau (Clode et al., 1999; Garwin, 2002). The dominance of clay minerals in the central biotite zone likely represents a sensitive response to the late-stage sericite/paragonite and intermediate argillic alteration overprints (Fig. 2; Garwin, 2002). It is unsurprising that biotite was not identified in the spectra given its remarkably low reflectance (Cudahy et al., 2001) especially when occurring alongside highly reflective smectites. However, vermiculite, which can form from hydrothermal alteration of biotite, was identified. The presence of chlorite in the biotite zone, and its dominance (alongside epidote) in the propylitic zone are consistent with expected propylitic alteration assemblages (e.g. Cooke et al., 2014a). Actinolite, where present, generally occurs in proportions too low to be detected. Zeolite minerals identified in distal samples have been previously noted and attributed to a final, low temperature, alteration stage (Clode et al., 1999).

Geochemical variation in chlorite has previously been recognised as an effective vector to mineralisation in the Batu Hijau system (Wilkinson et al., 2015). The major element geochemistry derived from electron microprobe analysis unsurprisingly matches that previously reported by LA-ICP-MS (Wilkinson et al., 2015) and shows that Mg# and Al:Si ratios in chlorite vary spatially with respect to the orebody. The lack of correlation between chlorite and whole-rock Mg# suggests that bulk rock composition is not a primary control of chlorite chemistry. An increase in chlorite Fe content away from the porphyry centre to a distance of ~1.5 km has been proposed to occur as a result of the outward advection and cooling of hypersaline brines enriched in Fe (Wilkinson et al., 2015). Al:Si ratios in chlorite vary as a result of substitution in the tetrahedral site (Deer et al., 2009) and are linked to fluid temperature (Cathelineau, 1988). Ca concentrations may be controlled by this reaction, and other major 2⁺ ions are also likely to be involved including Mg²⁺ and Fe²⁺, as well as trace elements such as Sr^{2+} .

These mineral chemical patterns are reflected in SWIR spectral features, especially those centred around 2250 nm and 2340 nm. It is well established that the chlorite Mg# influences the wavelength positions of these features, with more Fe-rich chlorites causing shifts to higher wavelengths (Yang and Huntington, 1996; Herrmann et al., 2001; Jones et al., 2005; Bishop et al., 2008), and this study confirms this relationship. Features in this region are all attributed to overtones of metal-OH bond stretching and bending (Hunt, 1977) which will be affected by the mass and/or ionic radius of the cations involved.

The apparent increase in absorption depths with decreasing Mg# in chlorite is not documented in any other study and may represent a new finding, but caution should be exercised with this interpretation. It is important to consider whether or not the Mg# is linked to increases in absorption depths, or if both factors are independently controlled by another variable that shows the same spatial pattern. If Mg# does directly control the absorption depth, this is postulated to be a result of the higher mass Fe cations having a stronger effect on the metal-OH bond stretches and vibrations.

An alternative explanation is that an increase in the abundance of chlorite in a sample causes an increase in the depth of its unique absorption features. This is because in any mixed (polymineralic) spectrum the prominence of a feature attributable to one mineral directly

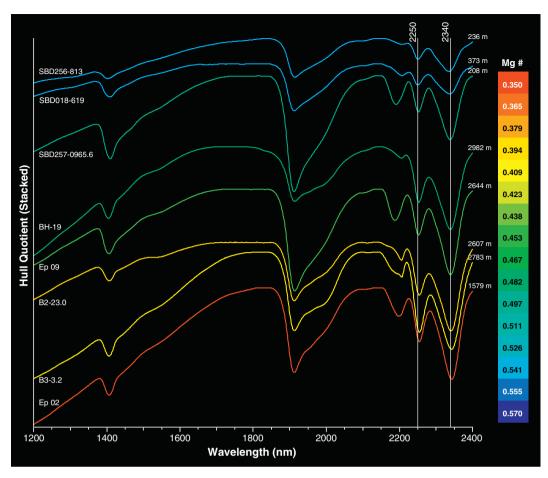


Fig. 13. Chlorite-dominated (hull-quotient corrected) spectra selected to illustrate changes in features. Spectra are stacked in order of the 2340 nm position and coloured according to Mg#. Distances from the sample site to the centre of the orebody are also labelled. Both the 2250 nm and 2340 nm features show a shift to higher wavelengths with decreasing Mg#. Feature depths also increase with increasing Fe content. A steepening of the hull between \sim 1400 nm and \sim 1900 nm is also observed as Fe content increases. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

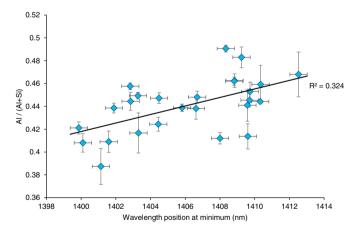


Fig. 14. Chlorite Al/(Al + Si) derived from EMP data plotted against the wavelength at the 1400 nm absorption feature minimum. A reasonably strong positive correlation is seen. Vertical error bars are 1σ standard error. Horizontal error bars are $\pm~0.5$ nm representing the measurement precision of the spectrometer.

depends on its proportion in the sample (Thompson et al., 1999; Herrmann et al., 2001). However, this explanation would contradict studies that have found chlorite abundance to decrease away from porphyry centres (Norman et al., 1991) rather than increase. In the Batu Hijau samples, the proportion of chlorite has not been accurately determined so that this possibly cannot currently be tested.

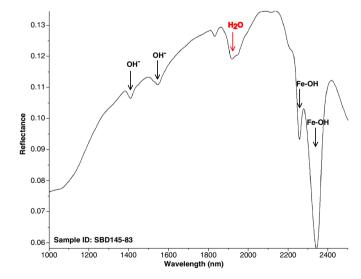


Fig. 15. SWIR spectrum of a sample predominantly made up of epidote. Diagnostic features include the deep Fe-OH absorption features at $\sim\!2250$ and $\sim\!2340$ nm, and the OH $^-$ absorption at 1550 nm.

The effect of mixed mineral assemblages on the SWIR spectra of rocks is perhaps the biggest problem encountered in this study. Although both spectral analysis techniques employ spectral unmixing at

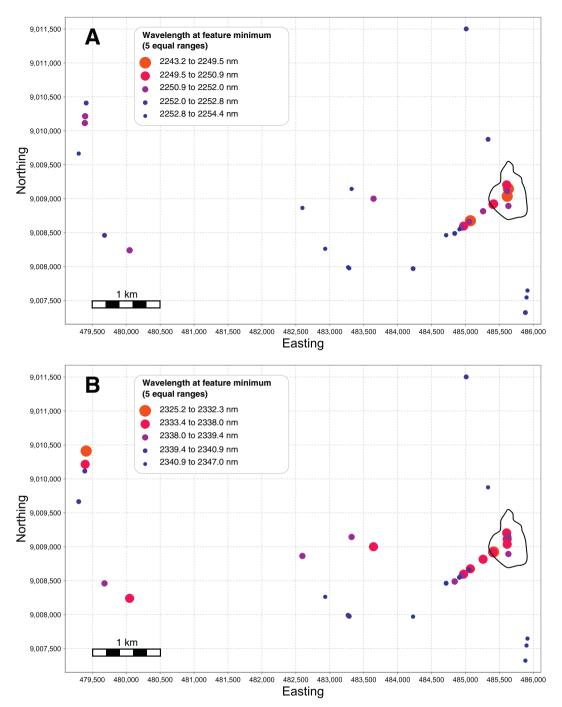
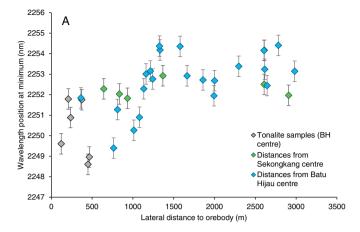


Fig. 16. Spatial variation of (A) the 2250 nm; and (B) the 2340 nm absorption feature positions in chlorite. Larger red circles correspond to shorter wavelengths. A systematic shortening of wavelength position is seen towards the centre of the Batu Hijau deposit along the south-west transect for both absorption features. This is also exhibited more weakly in the west towards the Sekongkang porphyry centre for the 2340 nm absorption feature. The 'strong biotite' alteration zone at Batu Hijau is outlined in black. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

their core, the effectiveness is limited – especially when the number of contributing minerals is high and when minerals have overlapping features. For example, the chlorite-epidote-calcite assemblage, which is common in porphyry systems, will have overlapping features in the region of 2340 nm (Dalton et al., 2004). At Batu Hijau, calcite is relatively rare and so presumably has little effect, however epidote is abundant, especially as the secondary mineral in chlorite-dominated spectra. This is likely to affect both of the important chlorite features at 2250 nm and 2340 nm.

In terms of wavelength positions, the narrower range of wavelength

positions that epidote-related absorptions occupy (Table 3) could create a bias in chlorite spectra towards more central positions in such samples. However, the fact that chlorite Mg# correlates with feature positions (Fig. 10) with the same trend as observed in previous studies on epidote-free samples (Yang and Huntington, 1996; Herrmann et al., 2001; Jones et al., 2005; Bishop et al., 2008) indicates that any epidote interference is limited. In terms of depth, the presence of epidote should deepen the 2340 nm absorption feature, which might explain the anomalously high absorption depth values in the plots demonstrating correlations between absorption depth and chemistry (Fig. 11). With



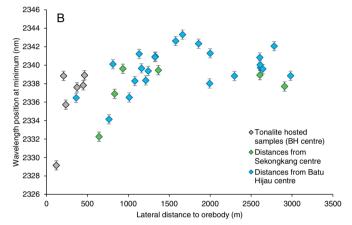


Fig. 17. Wavelength position at the minimum for (A) the 2250 nm; and (B) the 2340 nm absorption features in chlorite plotted against lateral distance to the nearest mineralised centre. Systematic increases are seen outwards to a distance of around 1.6 km with wavelengths decreasing slightly beyond this. Green points indicate samples with distances measured away from the Sekongkang centre rather than Batu Hijau. Grey points correspond to extremely proximal, mineralisation-hosting tonalite samples that are not strictly part of the propylitic halo and may represent a late overprint (see Wilkinson et al., 2015). Vertical error bars are \pm 0.5 nm reflecting the measurement precision of the spectrometer. Horizontal error bars are smaller than the symbol size (uncertainty in sample position is less than 10 m from GPS and the distance to ore estimate is thought to be accurate to within \sim 25 m). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

this considered, the absorption feature at 2250 nm is likely to be a better indicator of chlorite composition than that at 2340 nm. This point is also made in Herrmann et al. (2001) because the secondary Al-OH feature in white mica also overlaps the chlorite feature at 2340 nm. However, use of the 2250 nm feature may be limited in some deposits because it has been shown to completely disappear where there is pervasive weathering (Suryantini, 2003).

Two other spectral features were shown to vary with chlorite chemistry – the slope of the hull between 1400 nm and 1900 nm, and the position of the 1400 nm absorption feature. The increase in hull slope in more Fe-rich chlorite has been recognised previously (Thompson et al., 1999) and is attributable to the strong, broad absorption caused by electronic (charge transfer) effects in Fe²⁺ in the VNIR (Hunt, 1977; Clark et al., 1990). However, this feature occurs in many Fe-bearing minerals and so may just reflect an abundance of these in the rock, rather than a specific response to chlorite, thus explaining the lack of any strong systematic spatial variation. The 1400 nm wavelength position appears to relate to the Al:Si ratio in chlorite. Shifts in this absorption have been previously observed in chlorite (King and Clark, 1989) and are likely due to modification of the O–H vibration

frequencies as a result of the Tschermak substitution (Duke, 1994). Unlike the hull slope, this feature appears to offer considerable promise for use in exploration using field-portable or core-shed-based SWIR spectrometers. However, both features are inapplicable to satellite remote sensing due to strong atmospheric scattering effects at these wavelengths (Duke, 1994).

This study has been unable to conclude anything about potential mineral chemical controls on spectral variations of epidote due to a distinct lack of overlapping data: of the 16 samples that could be classified as epidote-dominated, only five had accompanying geochemical data. This is unfortunate because epidote has shown promise as a vectoring tool in porphyry deposits (Cooke et al., 2014b) and spectral variation across the epidote-clinozoisite solid-series is certainly recognisable (Roache et al., 2011). This is an area where future study would be useful.

6. Potential application to satellite remote sensing

The results from this study indicate that porphyry deposits could be targeted by using the absorption features at 2250 nm and 2340 nm which differ between Mg-rich chlorite that can be dominant in the inner propylitic zone (Wilkinson et al., 2015) and Fe-rich chlorite that can predominate further out, or which may be developed above buried porphyry systems (Halley et al., 2015). The precise wavelength positions can only be exploited, at present, using field spectrometers or hyperspectral sensors that are capable of collecting high-resolution spectra. It should therefore be possible to target porphyry deposits using hyperspectral imaging, and previous work has demonstrated the discrimination of Fe-chlorite from Mg-chlorite in hyperspectral data (Cudahy et al., 2001). However, the small wavelength shifts documented here are currently impossible to target using the broad bandwidths (0.02–0.2 µm) typical of satellite remote sensing.

Fortunately, the relative change in absorption feature depth is potentially recognisable using broad-band multispectral imagery collected by the ASTER (Advanced Spaceborne Thermal Emission Radiometer) satellite sensor. ASTER bands 7 and 8 measure surface reflectance in the ranges of 2235–2285 nm and 2295–2365 nm which individually span both absorption features of interest. Deeper absorption features should produce a darker (lower reflectance) response and ASTER band ratio images could perhaps be used to enhance these features.

7. Conclusions

SWIR reflectance spectroscopy is shown to be a powerful tool for characterising propylitic alteration associated with porphyry deposits. The collection of high resolution spectra using handheld spectrometers such as the TerraSpec 4, combined with matching algorithms such as those used by TSG and Halo, allows quick identification of spectrally-active minerals, even in the case of low-reflectance propylitic "greenrocks". From the spectra, chlorite and epidote were found to be the most abundant SWIR-active minerals in rocks from Batu Hijau, and are in greatest abundance in the more proximal propylitic zone. Spectral signatures from the biotite zone commonly indicate the presence of smectites and other phyllosilicates attributable to later stage, intermediate argillic and sericitic overprinting.

Chlorite chemistry can be utilised as a powerful vector to ore (Wilkinson et al., 2015) and this appears to translate to features in the SWIR spectra of chlorite-dominated samples. Chlorite from Batu Hijau varies significantly in terms of Mg#, which is likely the main cause of shifts in the wavelength position of absorption features at around 2250 nm and 2340 nm, and possibly the cause of depth variation in these features. The positions and depths of both features act as good vectors to mineralisation: wavelength positions shift from 2254 to 2249 nm and from 2343 to 2332 nm, and absorption depths decrease from around 35% to 5% respectively, moving from $\sim 1.6 \, \mathrm{km}$ to 500 m away from the orebody. This correlates with a general increase in the

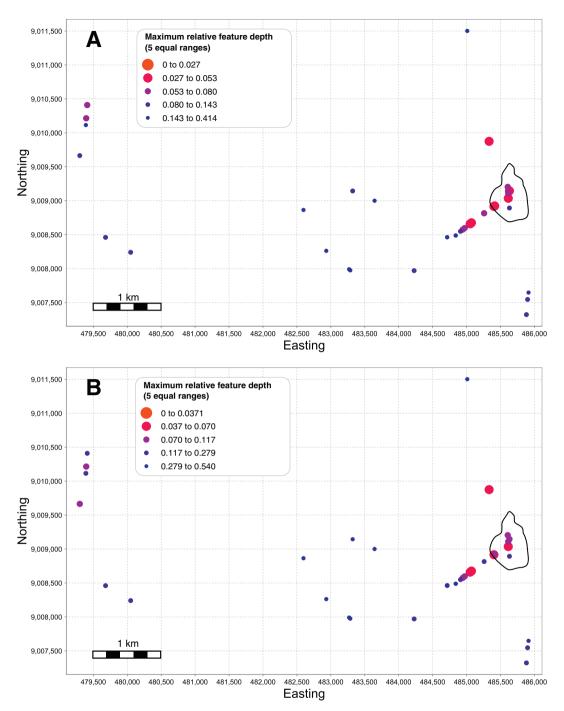
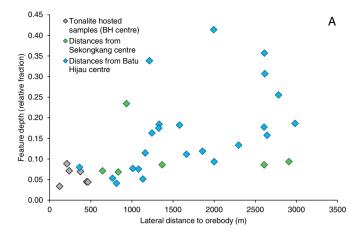


Fig. 18. Spatial variation of (A) the 2250 nm; and (B) the 2340 nm absorption feature depths in chlorite. Larger red circles correspond to shallower absorption features. A fairly systematic decrease is seen towards the centre of Batu Hijau along the south-west transect for both absorption features. No clear trend is observed towards the Sekongkang prospect. The 'strong biotite' alteration zone at Batu Hijau is outlined in black. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Mg# of chlorite from about 1.6 km towards the fringes of mineralisation. Absorption feature depth variations in particular seem to be a new finding and one potentially more applicable to remote sensing than the well-established position shifts because absorption depth changes can potentially be recognised by satellite remote sensing. The exact cause of changes in absorption depth is not entirely clear, but the fact that this can act as a vector to mineralisation is significant nonetheless, especially if these observations can be recognised in other porphyry systems.

The degree to which these findings apply to other porphyry deposits is still unclear. Furthermore, there is limited information at present to suggest that the variations in alteration mineral geochemistry are specific to fertile (well-mineralised) systems rather than weakly mineralised or barren ones. However, we do note that that the 2250 nm peak position and both 2340 nm and 2250 nm absorption feature depths do not appear to highlight the weakly mineralised Sekongkang prospect in the Batu Hijau district. Future work could include investigating chlorite spectral variation in other, variably mineralised, porphyry systems, and



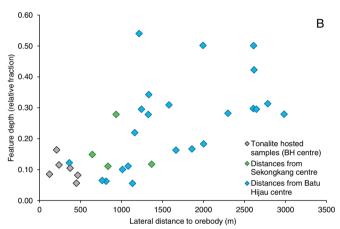


Fig. 19. Relative depths of (A) the 2250 nm; and (B) the 2340 nm absorption features in chlorite plotted against lateral distance to the nearest mineralised centre. A general deepening is observed moving away from the Batu HIjau centre, with slightly elevated values at around $1.3\,\mathrm{km}$ to $1.6\,\mathrm{km}$. Note that the same trend is not observed for the Sekongkang prospect, indicating possible utility as a discrimination tool.

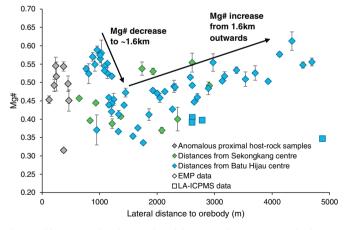


Fig. 20. Chlorite Mg# plotted against lateral distance to the nearest mineralised centre. The data show a sharp decrease in Mg content to a distance of around 1.6 km away from the centre, followed by a steady increase to what may be background levels. No significant relationship is seen in samples measured away from the Sekongkang centre (green). Vertical error bars are 1σ standard error. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

investigating in more detail the effects of epidote. We conclude that SWIR spectroscopy offers significant promise as a practical exploration tool in the "green-rock" environment.

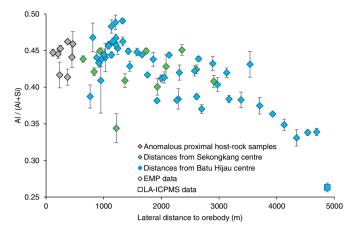


Fig. 21. Al/(Al + Si) content of chlorite plotted against lateral distance to ore. A systematic decrease is observed with distance from Batu Hijau that is not readily apparent in the Sekongkang data. Vertical error bars are 1σ standard error.

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