Mapping metamorphic hydration fronts with field-based near-infrared spectroscopy: Teakettle Junction contact aureole, Death Valley National Park (California, USA)

Edward F. Duke
Department of Geology and Geological Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakota 57701, USA

ABSTRACT

Mineral distribution in a previously undescribed contact aureole in siliceous dolomite at Teakettle Junction, Death Valley National Park (California, USA), was mapped with a handheld visible and near-infrared (Vis-NIR, 0.35–2.5 μm) spectrometer. With increasing distance from a small Jurassic (?) pluton, the following mineral zones occur: periclase (hydrated to brucite), forsterite (variably hydrated to serpentinite and typically accompanied by clinohumite), tremolite, and talc. Airborne Vis-NIR imaging spectrometer data with 5 m ground resolution shows serpentinite and tremolite distribution in close agreement with the field data. Field measurements show dolomite and calcite throughout the study area, along with minor amounts of phlogopite and illite. Hydrous minerals were detected in field measurements at levels on the order of 1 vol%.

Field measurements using Vis-NIR spectroscopy provide a direct and sensitive method for mapping metamorphic hydration fronts. Several distinct capabilities compared with conventional field and laboratory methods.

1. Acquisition of Vis-NIR spectra requires no sample preparation, and spectra can be acquired rapidly (20 s per sample in this study), so that many measurements can be made in a short period of time and high-spatial-density coverage is practical.
2. The diagnostic absorption features in Vis-NIR spectra that can be used for mineral identification are independent of grain size. This is important because many samples in contact aureoles are extremely fine-grained, making identification challenging in the field or even with optical microscopy.
3. Vis-NIR spectral measurements acquired in the field offer a link to airborne or spaceborne Vis-NIR imaging spectrometers.
4. Perhaps most importantly, Vis-NIR spectroscopy provides a direct and sensitive method for mapping the distribution of hydrous minerals, which serves to delineate patterns of infiltration of H₂O-rich fluids within contact aureoles.

Heterogeneity of fluid-rock interaction at this scale must be considered in models of heat and mass transfer accompanying contact metamorphism.

INTRODUCTION

Studies of contact aureoles in carbonate host rocks have been vital to the understanding of fundamental metamorphic processes such as heat transfer, fluid flow, and the interdependence of mineral reactions and volatile phase composition (e.g., Tracy and Frost, 1991; Ferry et al., 2002; Cui et al., 2003). Many basic processes of contact metamorphism may also scale to processes of regional metamorphic belts (Kerrick, 1991). Especially informative have been studies of contact metamorphism of siliceous dolomites, which undergo a well-established sequence of reactions involving hydration, dehydration, and decarbonation (Ferry, 1991). The primary record of these reactions is the distribution in the aureole of diagnostic CO₂- and OH-bearing minerals. As shown here, many of these minerals exhibit characteristic molecular absorption bands that enable reliable field-based identification with handheld visible and near-infrared (Vis-NIR) spectrometers. This paper describes the first systematic attempt to map mineral distribution in a contact aureole in siliceous dolomite based primarily on field Vis-NIR spectrometer measurements.

Field measurements using Vis-NIR spectroscopy were applied to map mineral distribution in a small, previously undescribed contact aureole near Teakettle Junction in western Death Valley National Park, California (USA). Most field measurements were acquired in a four-day period, yet the spectra provided reliable identification of the distribution of important mineral species and contact metamorphic zones. The results clearly delineate patterns of extensive hydration near the intrusive contact that are attributed to infiltration of H₂O-rich fluid of magmatic origin. In addition, the study area provides the opportunity to compare mineral distribution based on field-based Vis-NIR measurements with mineral distribution detected using airborne Vis-NIR imaging spectrometer data.

In addition to providing a field-based method for mineral identification, Vis-NIR spectroscopy offers several distinct capabilities compared with conventional field and laboratory methods.

1. Acquisition of Vis-NIR spectra requires no sample preparation, and spectra can be acquired rapidly (20 s per sample in this study), so that many measurements can be made in a short period of time and high-spatial-density coverage is practical.
2. The diagnostic absorption features in Vis-NIR spectra that can be used for mineral identification are independent of grain size. This is important because many samples in contact aureoles are extremely fine-grained, making identification challenging in the field or even with optical microscopy.
3. Vis-NIR spectral measurements acquired in the field offer a link to airborne or spaceborne Vis-NIR imaging spectrometers.
4. Perhaps most importantly, Vis-NIR spectroscopy provides a direct and sensitive method for mapping the distribution of hydrous minerals, which serves to delineate patterns of infiltration of H₂O-bearing fluids within contact aureoles.

Acquisition of high-spatial-density mineral maps, whether through field or remote-sensing
observations, can result is a more accurate characterization of the heterogeneity of mineral distribution, which is critical for realistic modeling of heat and mass transfer during metamorphism.

### GEOLOGIC BACKGROUND

The contact aureole discussed here is centered 2.5 km west-northwest of Teakettle Junction in western Death Valley National Park, California (Fig. 1). Burchfiel (1969) described a poorly exposed syenite stock at this location and noted that dolomite of the Cambrian Bonanza King Formation was metamorphosed to a very coarse-grained white (bleached) dolomite for ~120 m north of the contact. The southern and eastern portions of the pluton are covered by alluvial deposits, but the exposed portion indicates a minimum diameter of 2 km. Outside the contact aureole, the Bonanza King Formation consists of dark gray dolomite with some silty dolomite. North of the pluton, bedding in the Bonanza King Formation generally strikes subparallel to the contact contact aureole, the Bonanza King Formation generally strikes subparallel to the contact, striking east-west to northeast and dips homoclinal to the north at 20°–40°. However, near the pluton (approximately coincident with bleached zone), at distances of 300 m or less from the contact, there are several open to tight folds with axes that parallel the contact, and dips generally reverse, dipping south toward the pluton at 45° or more and locally vertical. The dip of the intrusive contact itself is not known.

Burchfiel (1969) reported a K-Ar whole-rock minimum age of 139 Ma and correlated the intrusion with the Cretaceous(?). Hunter Mountain Quartz Monzonite suite described by McAllister (1955, 1956). More recent age determinations for the Hunter Mountain suite range from late Permian to Middle Jurassic (Snow et al., 1991).

The Ubehebe Peak pluton (Fig. 1), which, like the pluton at Teakettle Junction, is considered to be part of the Hunter Mountain emplacement. Emplacement of the Ubehebe Peak pluton was dated at 173 ± 1 Ma (U-Pb zircon). With increasing distance from the contact, Roselle et al. (1999) mapped a discontinuous pericline zone and a local wollastonite zone, followed outward by forsterite and tremolite zones. Pressure at the time of metamorphism was estimated at 1.4–1.7 kbar on the basis of stratigraphic reconstruction, and pre-metamorphic temperature was estimated at ~300 °C. Subsequently, Kozak et al. (2004) examined the Ubehebe Peak aureole using remotely sensed data acquired with an airborne imaging spectrometer and backed up by >1000 field-based Vis-NIR spectra. The distribution of metamorphic minerals shown by the remote-sensing results was identical to the conventional isograd map of Roselle et al. (1999). However, in the remotely sensed Vis-NIR data, pericline and forsterite distribution was mapped on the basis of retrograde brucite and serpentine, respectively.

### SPECTROSCOPIC BACKGROUND

As used in this paper, “visible” (Vis) refers to the wavelength range 0.4–0.7 μm, and “near infrared” (NIR) refers to the wavelength range 0.7–3.0 μm (Clark, 1999). Reflectance spectroscopy of rocks and minerals in the visible and near infrared has developed over the past half century in parallel with advances in terrestrial and planetary remote sensing (e.g., Hunt and Salisbury, 1970; Hawthorne, 1988; Gaffey et al., 1993; Clark, 1999). Vis-NIR spectra of minerals are dominated by electronic processes (largely 0.35–1.5 μm) and molecular vibrational
processes (largely 1.0–2.5 μm). The Vis-NIR range is optimally suited for studies using reflected solar radiation, and absorption by Earth’s atmosphere is restricted to relatively narrow wavelength ranges. This is in contrast with the longer-wavelength NIR and mid-infrared region used in many laboratory-based Fourier transform infrared studies of minerals and silicate glasses (e.g., 2.5 to >25 μm). In parallel with developments in terrestrial remote sensing, portable field spectrometers have been developed for the purpose of ground-truthing remote-sensing data. Apart from their role in remote-sensing programs, these instruments are now used widely in ore deposit exploration because they can rapidly differentiate many diagnostic alteration minerals such as clay minerals and other phyllosilicates. This wide use, in turn, has led to the development of high-throughput, fully automated core-logging systems (e.g., Tappert et al., 2011) and on-the-fly spectral identification software for field spectrometers (Curtiss, 2013).

### Vis-NIR Spectral Features of Metamorphosed Siliceous Dolomite

Contact metamorphism of siliceous dolomite can be described by the CaO-MgO-SiO₂-CO₃-H₂O ± Al₂O₃ ± K₂O compositional system (Tracy and Frost, 1991). Minerals in this system that are distinctive in Vis-NIR spectra include the following minerals discussed in this paper: brucite, calcite, dolomite, phlogopite, serpentine, talc, and tremolite (see Table 1 for mineral formulas and abbreviations). These minerals contain CO₂ or OH functional groups that produce well-defined overtone and combination bands in the NIR region between 1.3 and 2.5 μm (Fig. 2; see also Clark et al., 1990; Clark, 1999). Additional minerals with diagnostic spectral features in this wavelength range include clinohumite or other minerals of the humite group, which can form as a result of fluorine metasomatism, and illite, which can occur in impure carbonate rocks. Although forsterite lacks CO₂ or OH absorption bands, it has a broad electronic absorption feature centered near 1.05 μm (Fig. 2A). On weathered surfaces, iron

### Table 1. Minerals Identified with Visible–Near Infrared (Vis–NIR) Spectroscopy

| Mineral or group | Formula | Wavelength of diagnostic features (μm) | Number of occurrences |
|------------------|---------|----------------------------------------|-----------------------|
| Brucite (Brc)    | Mg(OH)₂ | 1.299, 1.362, 1.397, 2.160, 2.318       | 26                    |
| Serpentine (Srp) | Mg₃Si₂O₅(OH)₃ | 1.283, 1.358, 1.390, 2.109, 2.130, 2.244, 2.272, 2.325 | 377                   |
| Forsterite (Fo)  | Mg₂SiO₄   | 1.050 (broad) | 211                    |
| Clinohumite (Chu)| 4Mg₂SiO₄·Mg(OH)₂F₂ | 1.439, 1.968, 2.214, 2.249, 2.309 | 101                   |
| Tremolite (Tr)   | Ca₂Mg₅Si₈O₂₄(OH)₂ | 1.393, 2.111, 2.298, 2.313, 2.383–2.385 | 60                    |
| Phlogopite (Phi) | KMg₃Al₂Si₅O₁₄(OH)₂ | 1.377, 2.245, 2.376–2.378 | 546                   |
| Talc (Tlc)       | Mg₃Si₂O₅(OH)₂ | 1.393, 2.077, 2.291, 2.313, 2.380–2.394 | 77                    |
| Illite (Ilt)     | ~K₀.₆₅Al₂.₆₅Si₃.₃₅O₁₀(OH)₂ | 1.413–1.417, 2.208–2.220 | 159                   |
| Calcite (Cal)    | CaCO₃     | 1.876, 1.994, 2.154, 2.335 | 285                   |
| Dolomite (Dol)   | CaMg(CO₃)₂ | 1.856, 1.976, 2.136, 2.318 | 483                   |

Notes: Bold values indicate the most diagnostic features in spectra of mineral mixtures; mineral abbreviations are after Whitney and Evans (2010).
hydroxides (e.g., goethite) can be detected at short wavelengths in Vis-NIR spectra (evident in spectra of dolomite, illite, and talc; Fig. 2A).

**ANALYTICAL METHODS**

Field Vis-NIR reflectance spectra were acquired at 145 sites in the contact aureole and in adjacent rocks that appeared to be weakly metamorphosed or unmetamorphosed. At each site, between five and 20 spectra were acquired within a 10 m radius, yielding a total of 946 spectral measurements. Generally, measurements were made on a freshly broken surface, but weathered surfaces gave similar results. In addition to field spectral measurements, 270 rock samples were collected for possible laboratory characterization.

Initial sample collection was conducted at 25 sites and samples were analyzed in the lab with a FieldSpec FR Pro backpack-mounted spectrometer (Analytical Spectral Devices, Inc.). Subsequently, field spectra were acquired at 120 additional sites with a TerraSpec Halo handheld spectrometer (Analytical Spectral Devices, Inc.). Both instruments cover the wavelength range 0.35–2.5 μm. This range includes both visible (Vis) and near infrared (NIR) wavelengths, but most mineral identification discussed here is based on features in the NIR region. Illumination in both instruments is provided by a high-intensity halogen lamp, and a reference panel of Spectralon is used as a reflectance standard. The TerraSpec Halo is operated in contact mode with internal illumination, and the analysis spot size is roughly 8 mm in diameter on the sample. In the case of the TerraSpec Halo measurements, acquisition time on the outcrop was 20 s, and the instrument displays real-time mineral matches based on an onboard spectral library of 153 minerals. In this study, however, final mineral identification was based on manual inspection with spectral analysis tools in ENVI software. Additional details on field spectrometer technical specifications are in the Appendix.

In order to evaluate the reliability of the spectral interpretations, 64 polished thin sections were examined using optical microscopy and by scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM-EDS). SEM-EDS was carried out with a Zeiss Supra40 variable-pressure field-emission SEM with an Oxford Instruments X-Max 80 mm² SDD energy-dispersive X-ray detector and AZtecEnergy microanalysis software. Typical operating conditions were 15 keV acceleration voltage and ~1.6 nA beam current. Mineral compositions were estimated using standardless quantitative analysis. Modal proportions of minerals in thin section were visually estimated from optical microscope and SEM examination.

In addition to characterization of sample mineralogy, eight rock samples were pulverized and analyzed for whole-rock CO₂ and H₂O content at LECO Technical Services Laboratory (St. Joseph, Michigan, USA) using a LECO RC-412 Multi Carbon Determinator. Powders were combusted in nitrogen on a 13 min temperature ramp from 110 °C to 1100 °C, and CO₂ and H₂O in evolved gases were analyzed with solid-state infrared detection cells. An additional set of 13 samples, including two from the previous set, were analyzed for H₂O content at ALS Geochemistry Analytical Lab (Vancouver, British Columbia, Canada). Samples were dried at 105 °C to remove surface moisture and then combusted at 1000 °C with infrared detection of H₂O in the evolved gas. Absolute differences in replicate measurements between the two sample sets were roughly 0.3 wt% at 9.0 wt% H₂O and 0.1 wt% at 0.3 wt% H₂O.

Field spectral measurements presented here are compared with airborne hyperspectral image data covering the western three-quarters of the study area. Airborne imagery was acquired with the HyMap airborne imaging spectrometer system (HyVista Corporation, Sydney, Australia). HyMap covers the reflected solar spectrum in 126 channels between 0.45 μm and 2.48 μm (Cocks et al., 1998), and for this acquisition, nominal ground resolution was 5 m. Because of absorption effects of atmospheric water vapor, the sensor does not collect data in the wavelength regions at 1.35–1.40 μm and 1.80–1.95 μm where absorption by water vapor is essentially complete. Calibrated radiance data were corrected for atmospheric absorption and converted to reflectance using the HyCorr correction procedure. The distribution of metamorphic minerals was generated in ENVI software using image-derived spectral end members and the mixture-tuned matched filtering (MTMF) algorithm (Boardman, 1998a). Additional details on HyMap acquisition, sensor specifications, image processing, and mineral mapping are in the Appendix.

**RESULTS**

**Mineral Identification and Distribution from Field-Based Vis-NIR Measurements**

Minerals identified in the Teakettle Junction contact aureole with Vis-NIR spectroscopy are listed in Table 1 along with ideal mineral formulas, wavelengths of diagnostic absorption bands used to identify each mineral, and the total number of occurrences of the mineral in the 946 spectra acquired in this study. Figure 2 shows representative rock spectra with diagnostic spectral features from Table 1 indicated by arrows. Spectra in Figure 2 have been continuum-removed and offset for clarity. Continuum removal (analogous to baseline correction) accentuates absorption features and suppresses effects of overall spectral background slope (Clark and Roush, 1984). Except for the spectra of brucite and tremolite, which are representative of essentially pure mineral end members, all other spectra in Figure 2 include spectral features of between two and four minerals (see figure caption for interpretation). Additional minerals identified with spectroscopy include goethite, hematite, kaolinite, and smectites; these are not discussed further because they are considered to be weathering products unrelated to the interpretation of contact metamorphism.

Minerals that were identified with optical microscopy or SEM-EDS, but that could not be identified reliably with Vis-NIR spectroscopy, include quartz or chert, diopside, K-feldspar, albite, spinel, Mg-chlorite, and trace accessory phases. Estimated modal concentrations for these are generally 1–2 vol% (less in the case of accessory minerals), although quartz content ranged to as much as 20 vol% and diopside content was estimated at 2–6 vol%. Diopside (CaMg₃Si₂O₆) was identified with SEM-EDS in eight samples,
Therefore, the discussion of metamorphic zones generally in association with forsterite. The principal Vis-NIR feature of diopside is a broad absorption centered near 1.0 μm (Adams, 1974), which is similar to the feature for forsterite, so it is possible that some samples identified as containing forsterite may include diopside.

The distribution of key minerals is shown in Figure 3. There is limited exposure of the aureole on the northwestern margin of the pluton, and the intrusive contact is covered by alluvium in the east. Therefore, the discussion of metamorphic zones will focus on the central part of Figure 3 where the contact is well located and where there is continuous outcrop of the aureole host rocks. Distances from the contact cited below are measured horizontally and may overestimate the true distance depending on the dip of the contact in the third dimension. Representative SEM images of samples from different metamorphic zones are shown in Figure 4. For reference, temperature versus mole fraction of CO₂ (T-XCO₂) relations for a subset of this system are shown in Figure 5.

The distribution of minerals determined by field-based Vis-NIR spectroscopy at 145 sites (946 spectral measurements) is summarized in this section, supplemented with information on modal abundance, grain size, and mineral chemistry based on 64 polished thin sections. Additional details on spectral identification of the minerals are included in the Appendix.

Brucite (Periclase Zone)

Brucite was detected at eight sites in the aureole, all within 50 m of the contact, and at two additional sites where small inliers of marble occur within the intrusion (Fig. 3A). Continuity of brucite occurrences at the contact cannot be established, similar to the finding of Roselle et al. (1999) in the nearby Ubehebe Peak aureole. Brucite occurs exclusively as a retrograde hydration product of periclase (MgO), and therefore the distribution of brucite is considered to define a discontinuous periclase zone. The periclase zone is typically the highest grade attained in contact metamorphism of siliceous dolomite (Fig. 5; also Ferry and Rumble, 1997). In the Ubehebe Peak aureole, Roselle et al. (1999) estimated the temperature at the periclase isograd at 620–665 °C.

Identification of brucite is considered highly reliable based on this study and that of Kozak et al. (2004) in which brucite distribution in the Ubehebe Peak aureole was mapped using both field and airborne Vis-NIR spectroscopy. However, as noted in Clark et al. (1990), brucite has very strong absorption between 2.1 and 2.4 μm, which can mask the presence of other mineral features in this wavelength range. The only other minerals identified in spectra of brucite-bearing samples were serpentine, phlogopite, and possible forsterite. Two brucite-bearing samples were examined with SEM-EDS, and these were from the same site. These contain 10–15 vol% brucite (pseudomorphs of periclase), calcite far in excess of dolomite, forsterite variably altered to serpentine, spinel, and trace accessories (geikielite, baddeleyite) (Fig. 4A).

Forsterite, Serpentine, and Clinohumite (Forsterite Zone)

In this work, forsterite, serpentine, and clinohumite are indistinguishable in terms of their spatial distribution (Fig. 3A). They occur along the contact and reach a maximum distance of 250–300 m from the contact. These sites are interpreted to represent the forsterite zone or a composite forsterite + clinohumite zone. This zone corresponds closely to the extent of bleaching and plastic deformation (or folding), similar to findings of Kozak et al. (2004) in the Ubehebe Peak aureole. Forsterite was tentatively identified in 211 spectra from 59 sites. SEM-EDS confirmed forsterite at 12 sites for which thin sections are available, and at all but one of those sites, forsterite was indicated in Vis-NIR spectra. Compositioanlly, SEM-EDS results indicate that the forsterite is nearly pure with Mg/(Mg + Fe) ≥ 0.99 and negligible Ca, Ti, or Mn.

All forsterite shows some degree of retrograde hydration to serpentine (Figs. 4A, 4B). In contrast to forsterite, which displays a single broad absorption feature, serpentine has numerous sharp Vis-NIR absorption features (Table 1; Fig. 2), and detection limits are estimated to be 0.5–1.0 vol%. Consequently, serpentine is considered to be a reliable proxy for forsterite distribution, and the occurrences of serpentine farthest from the intrusive contact are correlated with the forsterite isograd (see also Kozak et al., 2004). Serpentine was identified in 377 spectra from 75 sites, and all of those sites also had forsterite. All samples in which forsterite was confirmed by SEM-EDS show Vis-NIR features of serpentine. Serpentine modal abundances in these samples were estimated at 2–25 vol% with SEM-EDS.

Clinohumite can be difficult to distinguish from forsterite with optical microscopy or even with SEM-EDS in the absence of a distinct fluorine X-ray peak (Fig. 4B). However, clinohumite is very distinctive in Vis-NIR spectra (Fig. 2), and comparison with SEM-EDS results suggest detection levels of ~1 vol%. Clinohumite was identified in 101 spectra from 44 sites, most of which also had forsterite. Clinohumite modal abundances were estimated at 1–20 vol% with SEM-EDS, with most samples containing >5 vol%. SEM-EDS detection of fluorine content is not accurate enough to distinguish reliably between members of the humite group; however, Mg/Si values are in the range 2.2–2.3, consistent with the stoichiometry of clinohumite or humite. Only traces of Ti or Fe were detected.

Tremolite and Talc (Tremolite and Talc Zones)

Tremolite was identified in 60 spectra representing 26 sites. Talc was indicated in 77 spectra also representing 26 sites, 11 of which also had tremolite. Vis-NIR spectra of tremolite and talc are sufficiently similar that it can be difficult to differentiate between them when present as minor phases in a rock (see Appendix for details on identification). Tremolite occurrences generally lie between 100 m and 350 m from the contact, whereas talc occurrences begin slightly farther from the contact, between 150 m and 200 m, and extend to at least 500 m from the contact (Fig. 3B). Although the location of the contact is not well known in the eastern part of the study area, it is likely that some of the talc occurrences there are at least 800 m
Figure 3. Mineral distribution in Teakettle Junction aureole based on visible–near infrared (Vis-NIR) spectra. Small black circles show location of all 145 sites. Contact shown between intrusion and host rocks of the Bonanza King Formation. (A) Inner aureole (brucite after periclase, forsterite, clinohumite, serpentine after forsterite). Ji—Jurassic (?) intrusion; Cbk—Cambrian Bonanza King Formation; Qal—Quaternary alluvium; TkJ—location of Teakettle Junction (road junction). Dashed line shows limit of serpentine (Srp) and forsterite (Fo). (B) Outer aureole (tremolite and talc). (C) Illite and phlogopite distribution. Base image: WorldView-2 (DigitalGlobe), acquired 12 December 2012. See Figure 1 for regional geologic setting.
from the contact and possibly >1200 m from the contact, and these occurrences are confirmed with SEM-EDS. For example, the occurrence of talc at the site in the extreme eastern part of Figure 3B is confirmed by SEM-EDS. Because talc is present throughout the sampled area, it is not possible to define a talc-in isograd.

Tremolite modal abundances were estimated at 1–10 vol% with SEM-EDS, and tremolite was identified with Vis-NIR at levels estimated as low as 2 vol%. Figures 4C and 4D show SEM images of tremolite- and talc-bearing samples. Talc modal abundances were estimated at 3 vol% or less (one exception with 6 vol%) with SEM-EDS, and talc was identified with Vis-NIR at levels estimated at 1 vol% or less. In the case of talc, the grain sizes are generally very small (<30 μm), and talc may be easily overlooked in routine SEM examination. Compositionally, SEM-EDS results indicate that tremolite contains variable Al, Na, K, Ti, and F (only trace Fe), and talc contains minor Na, Al, and F. Fluorine is present in these minerals throughout the study area and does not appear to be related to proximity to the intrusion.

Phlogopite and Illite

Phlogopite was detected in Vis-NIR spectra at 136 of the 145 sites (546 spectra), ranging from the inner aureole to the most distal sites (Fig. 3C). Therefore, delineating a phlogopite-in isograd within the sampled area is not practical, and phlogopite occurrences in the outer aureole possibly date to an earlier regional event as suggested by Roselle et al. (1999). Illite occurs at 50 sites (159 spectra) and although it was identified at a few locations in the inner aureole, illite is nearly ubiquitous at sites outside the forsterite isograd. Figures 4D–4F show SEM images of phlogopite- and illite-bearing samples.

Phlogopite was identified in 50 samples with SEM-EDS, and in 48 of these, phlogopite was also indicated by Vis-NIR. In samples examined with SEM-EDS, modal abundances of phlogopite were estimated to range from <1 vol% to 8 vol%, and phlogopite was correctly identified with Vis-NIR at levels estimated at <1 vol%. SEM-EDS indicates that phlogopite is typically <20 μm in length and phlogopite- and illite-bearing samples.

Phlogopite was identified in 50 samples with SEM-EDS, and in 48 of these, phlogopite was also indicated by Vis-NIR. In samples examined with SEM-EDS, modal abundances of phlogopite were estimated to range from <1 vol% to 8 vol%, and phlogopite was correctly identified with Vis-NIR at levels estimated at <1 vol%. SEM-EDS indicates that phlogopite is typically <20 μm in length and phlogopite- and illite-bearing samples.

Illite was identified in nine samples with SEM-EDS, and in eight of those, illite was also identified with Vis-NIR. However, there were nine additional samples in which illite was not noted with SEM-EDS analyses but for which Vis-NIR clearly indicated illite. Illite modal abundances were estimated at
2 vol% or less, and illite was correctly identified with Vis-NIR at levels estimated at <1 vol%. It is possible that at these low modal abundances and with grain sizes <20 μm, Vis-NIR may be more sensitive than SEM-EDS for detecting illite in the absence of careful SEM examination. SEM-EDS analysis shows that most illite is Mg rich, which is consistent with the observed relatively long wavelength of the 2.2 μm band (Clark, 1999; Duke and Lewis, 2010). SEM-EDS examination showed that whereas most illite is very fine grained (<20 μm), samples from the three most distal sites included larger flakes (50–200 μm) interpreted to be detrital muscovite.

Dolomite and Calcite

Dolomite and calcite are the dominant minerals in all samples, accounting for a minimum of 60 vol% based on petrographic examination and SEM-EDS. Yet, dolomite and calcite were identified with Vis-NIR spectroscopy in only 73% of the samples. This underrepresentation stems from the fact that the principal absorption bands at 2.318 μm for dolomite and 2.335 μm for calcite can be masked by relatively small amounts of brucite or hydrous silicates, all of which absorb strongly between 2.25 μm and 2.35 μm (Table 1; Fig. 2C). In some cases, dolomite and calcite can be identified on the basis of minor bands between 1.856 μm and 2.154 μm (Fig. 2A), but these bands are not always evident. Because the distribution of dolomite and calcite is not fundamental to the interpretation of contact metamorphism, these minerals are not discussed further except to note that there is a tendency for both dolomite and calcite to occur in the bleached inner aureole (inside the forsterite isograd) but for dolomite alone to occur in the darker and more distal units in the north-central and eastern parts of the study area (outside the tremolite isograd). That distribution is consistent with the progressive increase in the ratio of dolomite to calcite shown in the sequence of SEM images (Figs. 4A–4F). For example, calcite (bright in backscattered electron images) is abundant and dolomite is subordinate in Figures 4A and 4B, which are from the inner aureole. Conversely, calcite is absent or occurs in only trace amounts in Figures 4E and 4F, which are from the outer aureole or unmetamorphosed rocks. Figures 4C and 4D contain tremolite and talc, respectively, and show intermediate ratios of calcite and dolomite. Progressive increase in calcite and decrease in dolomite with increasing temperature of metamorphism is predicted by the phase relations in Figure 5.

Other Minerals

Minerals identified with SEM-EDS but not identified with Vis-NIR spectroscopy include quartz or chert, K-feldspar, albite, and chlorite. These minerals are all found outside of the tremolite zone with the exception of two examples of quartz with tremolite and four examples of chlorite with tremolite. Trace accessory minerals (<0.1 vol%) were also not identified with Vis-NIR.

Airborne Vis-NIR Mineral Mapping

Field Vis-NIR spectrometers are widely used to correlate remotely sensed spectral measurements with outcrop- and sample-scale spectral measurements. This type of comparison is possible in the Teakettle Junction contact aureole because bedrock exposure is good and airborne imaging spectrometer data are available covering most of the study area. HyMap image data for the Teakettle Junction aureole cover essentially the same wavelength range as that covered by the field spectrometers used in this study; however, ground resolution of the HyMap data is estimated at 5 m, and absorption effects from atmospheric water vapor prevent collection of useful data in spectral regions at 1.35–1.40 μm and 1.80–1.95 μm. The spectral resolution and spectral sampling interval for the airborne system are also significantly poorer than in the case of the field spectrometers, so fine spectral details are not recorded as well as with the field instruments. In practice, the region between 2.05 and 2.45 μm exhibits the most diagnostic spectral features for identification of minerals in the CaO-MgO-SiO₂-H₂O-CO₂ system (Fig. 2C). Figure 6 shows a comparison of HyMap image-derived spectra and

Figure 5. Simplified temperature versus mole fraction of CO₂ (T-Xₑₒ₆) diagram for system CaO-MgO-SiO₂-H₂O-CO₂ at 1.5 kbar (modified from Davidson and Haileab, 2004). Reactions involving diopside and serpentine excluded for simplicity. Phlogopite, clino- humite, and K-feldspar compositions lie outside this system (see Moore and Kerrick, 1976). Mineral abbreviations: Brc—brucite; Cal—calcite; Dol—dolomite; Fo—forsterite; Per—periclase; Qz—quartz; Tlc—talc; Tr—tremolite.

Figure 6. Comparison of HyMap image-derived spectra and field spectra for tremolite (Tr) and serpentine (Srp) in the 2.05–2.45 μm wavelength range. Spectra have been normalized for continuum effects and offset vertically for clarity. Distinctive absorption features are indicated with arrows. Labeled wavelengths correspond to HyMap band centers. See text for additional discussion.
field spectra for tremolite and serpentine in the 2.05–2.45 μm wavelength range. The field spectra are from an 8-mm-diameter spot on samples, whereas the HyMap data represent the average spectrum of a 5 m pixel. The sampling interval for HyMap spectra is roughly 17 nm, compared with 1.4–2.0 nm for field spectra (resampled to 1 nm), so the HyMap spectra appear jagged. Although the resolution of the airborne spectral data is poor compared to the field data, diagnostic absorption features are still evident, and these can be used to generate mineral maps. For example, the HyMap spectrum for tremolite shows a diagnostic feature at 2.382 μm as well as a slight shoulder or left asymmetry between HyMap bands at 2.298 and 2.315 μm in the region where tremolite exhibits a doublet. Phlogopite on the other hand has an absorption closer to 2.376 μm and a feature at 2.245 μm (Fig. 2C) that is not observed in the HyMap spectra. The HyMap spectrum for serpentine shows diagnostic features between HyMap bands at 2.104 and 2.140 μm, and the asymmetry between HyMap bands at 2.246 and 2.332 μm is also consistent with the serpentine field spectrum.

Figure 7 shows the distribution of serpentine and tremolite derived from mixture-tuned matched filtering (MTMF) compared to field-based occurrences of the minerals (Figs. 3A, 3B). Registration of the HyMap image pixels appears good in most parts of Figure 7, although there are some locations where there appear to be registration errors of as much as 15 m. The overall distribution of serpentine and tremolite based on the HyMap data is consistent with the distribution based on field data (Fig. 7). However, processing of the HyMap data was performed after field work was completed; therefore, some locations where the HyMap data indicate significant tremolite were not sampled and cannot be confirmed by field data (e.g., near the eastern edge of Fig. 7, location “b”). It is noteworthy that the HyMap data indicate that the occurrence of these two minerals is variable within their respective zones, which is consistent with field observations. For example, in the case of tremolite, the image shows areas in the north-central part of Figure 7 (location “a”) where tremolite occurs preferentially in specific bedding units, also consistent with field observations. As discussed previously, tremolite and talc have similar spectra. Considering the poorer spectral resolution of the HyMap data, it is therefore possible that some pixels classified as tremolite may contain talc. The map distribution, however, is more consistent with the distribution of tremolite shown by field spectra and SEM-EDS. Also, tremolite is generally much more abundant than talc in samples that contain these minerals, so it is more likely that the remote-sensing data are detecting tremolite.

Although not shown here, HyMap mineral maps were also generated for calcite and dolomite in the inner parts of the contact aureole. In the outer aureole and unmetamorphosed rocks, the Bonanza King Formation is darker owing to a higher content of reduced carbon. Reduced carbon, even in trace amounts, absorbs strongly across the Vis-NIR range (Crowley, 1986). As a result, attempts to map calcite and dolomite in the darker portions of the outer aureole and in unmetamorphosed rocks were largely unsuccessful.

For the remaining minerals identified in field spectra (Fig. 2), it has not been possible to generate HyMap mineral maps. Although Kozak et al. (2004) were able to map the distribution of brucite in the Ubehebe Peak aureole using HyMap data, it has not been possible to make a similar map for the Teakettle Junction aureole. The extent of brucite-bearing marble in the Teakettle Junction aureole is limited, so the number of pixels containing brucite is
correspondingly small. In the case of phlogopite, identification in remotely sensed imagery is challenging because the diagnostic absorption band at 1.377 μm (Fig. 2B) lies in the region of atmospheric water vapor absorption at 1.35–1.40 μm. In the case of forsterite, the diagnostic feature near 1.05 μm is broad and shallow, and partly overlaps with features of goethite (Fig. 2A). Remote detection of talc and illite is limited by the low modal abundances of these minerals (generally <2 vol%). Clinohumite absorption features at 2.214 and 2.249 μm are potentially useful for identification in remotely sensed imagery but have not been detected in this study.

Vis-NIR Spectra and Metamorphic Hydration

Vis-NIR spectroscopy provides a direct and sensitive method for detection of OH-bearing phases. Hydrous minerals have a prominent NIR absorption band near 1.4 μm that is assigned to the first overtone of the OH stretching vibration (Fig. 2). It should be noted that structurally bound H₂O results in absorption near 1.9 μm; however, it can also contribute to broad absorption near 1.4 μm (Clark et al., 1990). Although none of the minerals discussed here contains structural H₂O, minor amounts of adsorbed water may occur. In the following discussion, it is assumed that the depth of the absorption band near 1.4 μm is largely a function of the OH content of minerals in the sample and that any contribution from H₂O is minor. Unpublished Vis-NIR spectra of powder mixtures of pure dolomite and pure serpentine indicate that the serpentine OH band (shown at 1.390 μm in Fig. 2) can be detected at serpentine concentrations as low as 0.1 wt%. Other studies have reached similar conclusions regarding the sensitivity of NIR spectroscopy for detecting trace amounts of OH-bearing minerals in silicate and carbonate rocks (e.g., Zhang et al., 2001; Murphy et al., 2017). Although this band is not detected in remotely sensed spectra because of absorption by atmospheric water vapor, the depth of this OH absorption band is readily quantifiable using field or lab spectrometers. These spectrometers use an internal light source and operate in direct contact with the sample, which eliminates the atmospheric path for both incident and reflected radiation.

In this section, a greater depth of the OH band is interpreted to reflect a greater proportion of OH minerals and therefore a greater whole-rock H₂O content. In order to explore this relationship, 19 samples from this study showing a range in the 1.4 μm OH band depth were selected for whole-rock H₂O analyses. Here, the value of the OH band depth was calculated from the continuum-removed spectrum in the wavelength range between 1.2 μm and 1.6 μm. Because the value of the continuum is 1, the band depth is given as 1 minus the value at the reflectance minimum. The inset in Figure 8 illustrates examples of spectra with band depths of 0.04, 0.13, 0.28, and 0.64 calculated in this fashion. The main part of Figure 8 shows the relationship between OH band depth and whole-rock H₂O content. Fields of characteristic hydrous minerals detected with Vis-NIR are labeled.

Hydrous phases in unmetamorphosed rocks and the outermost aureole are predominantly phlogopite and illite (± tremolite and talc). Stoichiometric H₂O content for these phases ranges from roughly 2 wt% to 4 wt%, and modal abundances for these phases rarely exceed 3 vol%, especially in the unmetamorphosed rocks. Figure 8 (main figure) shows five such samples, and these have the lowest OH band depth values and whole-rock H₂O content of 0.01–0.34 wt%. Hydrous phases in the inner aureole are predominantly serpentine ± clinohumite and phlogopite. Stoichiometric H₂O content for these phases ranges from ~2 wt% for clinohumite (depending on OH/F) to 12 wt% for serpentine, and modal abundances for each are generally >5 vol%, and in cases exceed 20 vol%. Figure 8 shows twelve such samples, and these have OH band depth values of 0.1–0.7 and whole-rock H₂O content of 0.12–5.37 wt%. Two brucite-bearing samples are shown in Figure 8. Stoichiometric H₂O content for brucite is 31 wt%, and brucite modal abundance in the samples is estimated at 10–15 vol% along with ~8 vol% serpentine and traces of phlogopite. The OH band depth values for these samples are 0.63–0.64, and the whole-rock H₂O contents are 8.90–9.09 wt%. The lowermost spectrum in the inset in Figure 8 shows the brucite-bearing sample with OH band depth of 0.64 (also shown in the SEM image in Fig. 4A).

The relationship between OH band depth and whole-rock H₂O content (Fig. 8) provides overall support for the contention that OH band depth is an indicator of the degree of hydration of the rocks in this study. There is, however, significant scatter in the data. Several factors may contribute to the observed scatter. Band depth is easily computed from the spectra, but the integrated area of the OH absorption feature (or features, in the case of multiple bands) would presumably provide a better measure than the depth at a single wavelength (the wavelength corresponding to the reflectance minimum in the simple formulation used here). In detail, some minerals have complex spectra with multiple bands in this region, and most spectra have OH features resulting from several minerals in this range (Fig. 2B; Fig. 8 inset). Moreover, the relationship between absorption band depth and structurally bound OH may be different for different minerals depending on crystal chemical differences.
and properties of mineral mixtures such as grain size and albedo also affect this relationship (Mil-likien and Mustard, 2007a, 2007b). But even lacking a quantitative relationship between OH band depth and the hydration state of rocks, the measurement is simple and provides qualitative information on H₂O content without the need to perform explicit spectral identification of all hydrous phases. The approach is widely applicable in fields beyond contact metamorphism, including exploration for hydrothermal ore deposits and searching for past aqueous environments on Mars.

**Variation in OH Band Depth within the Aureole—Evidence for a Metamorphic Hydration Front**

The data from a subset of 19 samples presented above and shown in Figure 8 establish overall correlations among OH band depth, whole-rock H₂O content, and occurrence of hydrous minerals in the aureole. In order to place these relationships in a spatial context, Figure 9 illustrates the variation in OH band depth at all 145 sites in the aureole. Figure 9 shows the distribution of samples using a band depth of 0.2 as a first-order discriminator between samples with relatively low hydration and relatively higher hydration. Note that each site includes multiple samples with varying OH band depth values, and the map symbols in Figure 9 indicate only the maximum OH band depth for the site. As an example of variation at a site, one site with five samples has OH band depths that range from 0.04 in a sample that contains only calcite and dolomite to 0.64 in a sample that contains brucite, serpentine, and phlogopite in addition to calcite and dolomite (the latter is one of the brucite-bearing samples in Fig. 8).

The OH band depth of 0.2 is used to discriminate low and high levels of hydration following the results shown in Figure 8. With one exception, samples with band depth <0.2 have whole-rock H₂O content <0.5 wt% (>82% of the 946 samples have band depth <0.2). Samples with band depth >0.2 in Figure 8 generally have whole-rock H₂O content >0.5 wt% (<18% of total samples). Sites with OH band depths >0.2 are restricted to distances within ~300 m from the contact in the central part of the aureole where the contact is well exposed (Fig. 9). The outer limit of these values is effectively the same as the serpentine (forsterite) isograd. This observation follows directly from the previous discussion of the correlation between band depth and mineral occurrence in connection with Figure 8.

To illustrate more clearly the variation in OH band depth at individual sites and with respect to distance from the intrusive contact, two profiles were constructed and are shown in Figure 10. Locations of the profiles are shown in Figure 9. The profiles are approximately perpendicular to the contact and to inferred isograds. Band depth values for samples within 200 m on either side of the profiles were projected onto the profile. Note that the contact is well exposed for the western profile (B–B′, Fig. 10), but the location of the contact is not known for the eastern profile (A–A′, Fig. 10) and distances along A–A′ are measured from the limit of outcrop.

In contrast to the map (Fig. 9), which reflects only the maximum OH band depth at each site, the profiles in Figure 10 highlight the wide variation in OH band depth that characterizes all sites. The profiles (especially A–A′, Fig. 10) also reveal the abrupt decrease in OH band depth values that occurs at distances beyond the serpentine (forsterite) isograd. Moreover, there is no clear indication of a gradient with respect to distance from the contact. Sites inside the serpentine isograd include a large proportion of band depth values >0.2, but there is no clear pattern within this zone. Outside the serpentine isograd, band depths are exclusively <0.2 at all sites. The indication of an abrupt change in the hydration state of the rocks at the serpentine (forsterite) isograd suggests that this boundary marks a hydration front. At greater distances from the pluton, the hydrous phases tremolite and talc occur in the outer aureole. However, stoichiometric H₂O content is roughly 2 wt% for tremolite and 5 wt% for talc, and modal abundances rarely exceed 5 vol% for tremolite and 5 vol% for talc.
These observations, along with the information in Figures 8–10, suggest that rocks in the outer aureole underwent little or no interaction with external H$_2$O-rich fluid during metamorphism. Minor amounts of phlogopite and illite also occur beyond the serpentine (forsterite) isograd; however, as noted previously, phlogopite may result from an earlier regional metamorphic event, and illite likely results from sedimentary or diagenetic processes. The proposed hydration front also marks the maximum extent of bleaching in much of the aureole. In a study of bleached limestones in the Notch Peak contact aureole (Utah), Todd (1990) concluded that the mobilization of reduced carbon (bleaching) was an extremely sensitive indicator of the maximum extent of infiltration of H$_2$O-rich fluids.

It should be noted that one site with brucite is projected on to profile B–B’ (Fig. 10), and a possible brucite (periclase) zone is indicated. However, the OH band depth for this sample is only slightly above 0.2, which is unusually low for a brucite-bearing sample (compare brucite samples in Fig. 8 with band depth of >0.6). The Vis-NIR identification of brucite at the site near profile B–B’ was highly questionable, and a thin section is not available. It is therefore possible that brucite is absent or occurs at very low abundance, and this might explain the low OH band depth value for this sample in Figure 10.

**DISCUSSION**

Mineral distribution in the Teakettle Junction aureole determined with field Vis-NIR spectroscopy follows established patterns for contact metamorphism of siliceous dolomite. The sequential occurrence of brucite (periclase), serpentine (forsterite), tremolite, and talc at increasing distance from the intrusive contact is consistent with decreasing temperature in the CaO-MgO-SiO$_2$-CO$_2$-H$_2$O system, shown in simplified form in Figure 5. Although smaller in spatial extent, the sequence of mineral zones presented here is the same as that in the massive dolomite assemblage at Alta, Utah (Moore and Kerrick, 1976). More detailed reactions involving clinohumite are discussed in Moore and Kerrick (1976), and retrograde formation of brucite and serpentine is discussed in Ferry and Rumble (1997) and Ferry (2000).

On the other hand, mineral distribution in the Teakettle Junction aureole differs slightly from that in the nearby Ubehebe Peak aureole (Roselle et al., 1999); no humite minerals were mapped at Ubehebe Peak, and talc distribution was not specifically addressed in that study. The Teakettle Junction aureole is also smaller in spatial extent than the Ubehebe Peak aureole. At Ubehebe Peak, the forsterite isograd is 750 m from the contact, compared

![Figure 10. Profiles showing variation in OH band depth (given as 1 minus value at reflectance minimum) with distance from intrusive contact based on field visible–near infrared (Vis-NIR) measurements (see Fig. 9 for location of profiles). Solid squares indicate individual samples, and vertical lines connect samples from same site. Approximate horizontal ranges of mapped mineral zones are indicated above data points (Brc—brucite; Srp—serpentine; Tr—tremolite; Tlc—talc). Note that in B–B’, contact is well exposed, and distances are measured from contact; in A–A’, contact is not exposed, and distances are measured from southern limit of outcrop.](http://pubs.geoscienceworld.org/gsa/geosphere/article-pdf/17/1/306/5217485/306.pdf)
Conclusions

This study demonstrates that field-portable Vis-NIR spectrometers can provide rapid, situ identification of mineral distribution in metamorphosed siliceous dolomite. Hundreds or thousands of georeferenced measurements can be acquired in the field, from which a subset of samples can be retained for more expensive and time-consuming laboratory analyses. Additionally, these data provide ground truth for remotely sensed Vis-NIR observations. With the rapid expansion of drone-based hyperspectral imaging systems with spatial resolution of a few centimeters and integrated lidar detection, remote-sensing applications exist that can yield unprecedented high-resolution maps of contact aureoles such as that at Teakettle Junction.

For the 10 minerals discussed here, the spatial distribution determined with field-based spectral measurements collected in a four-day period is identical to the distribution based on subsequent

to the estimate of 250–300 m for the Teakettle Junction aureole. Two factors likely contribute to this difference in scale. First, the intrusive body at Teakettle Junction appears to be much smaller than the Ubehebe Peak pluton (Fig. 1). Second, at Ubehebe Peak, bedding in the host rocks strikes directly into the intrusive contact, which may have promoted heat transfer and fluid flow along these structures. At Teakettle Junction, bedding and formation contacts are essentially parallel to the contact, potentially impeding heat transfer and fluid flow (Ferry et al., 2002).

The presence of brucite (after periclase) in contact aureoles is considered unequivocal evidence for infiltration of H$_2$O-rich fluid (Moore and Kerrick, 1976; Ferry and Rumble, 1997; Ferry et al., 2002). For example, Figure 5 shows that under realistic temperature conditions of contact metamorphism, periclase and brucite are stable only at very low values of X$_{CO_2}$ (i.e., high X$_{H_2O}$). Similarly, humite-group minerals indicate interaction with fluorine-rich fluids of likely igneous origin. This study demonstrates the ability to map the distribution of these and other minerals with field spectrometers in real time and while at the outcrop. Improved understanding of the distribution of these minerals can lead to new insights into the processes of heat and mass transfer in contact aureoles.

Perhaps more important than confirming fluid infiltration, the use of field spectrometers allows acquisition of hundreds or thousands of closely spaced measurements that may help delineate the geometry of fluid flow and locations of chemical or hydration fronts at a scale appropriate to natural processes. For example, models of coupled fluid flow and chemical reaction in contact aureoles imply that fluid flow is extremely heterogeneous and predict that isograd geometry may be highly irregular (on the scale of 10 m or less) with sharp discontinuities or reaction fronts (Marchildon and Dipple, 1998; Cook and Bowman, 2000). Conventional maps showing generalized metamorphic zones and isograds ignore the complexity and heterogeneity of mineral distribution and mineral abundance, and this, in turn, hinders a realistic interpretation of processes controlling the distribution of fluid flow and the driving mechanisms of mineral reactions.

Roselle et al. (1999) presented stable isotope evidence for heterogeneous fluid infiltration in the Ubehebe Peak aureole. In their study of >400 samples, they found depleted $^{18}$O and $^{13}$C values exclusively within 850 m of the intrusive contact, effectively inside their forsterite isograd. Importantly, they found that within that zone, fewer than one-quarter of the samples showed clear evidence of isotopic exchange with externally derived fluids. The results of the current study in the Teakettle Junction aureole point to similar processes of fluid infiltration on the basis of field spectral measurements. Figures 9 and 10 show that hydration of aureole rocks is effectively limited to samples inside the serpentine (forsterite) isograd, near which there is a sharp hydration front. Within this zone, however, the extent of hydration is highly variable, even at individual sample sites with samples spaced on the order of 1 m or less. This study does not resolve the factors underlying the heterogeneous hydration of samples; local differences in the extent of hydration may be caused by heterogeneous fluid flow or by variations in bulk rock composition between bedding units. For example, formation and preservation of hydrous minerals may be favored in bulk compositions with higher Mg/Ca (Ferry and Rumble, 1997). Regardless of the cause, the results of this study and others (Roselle et al., 1999; Cook and Bowman, 2000) imply that heterogeneity of fluid interaction must be considered in models of heat and mass balance in contact aureoles.

The distribution of hydrous minerals shown in this study provides evidence for a sharp hydration front in the Teakettle Junction aureole, but it does not explain the timing of fluid infiltration or source of fluid. Ferry and Rumble (1997) studied fluid flow during contact metamorphism in periclase marble at Silver Star, Montana (USA), and Beinn an Dubhaich, Scotland (UK), applying phase equilibrium considerations and oxygen isotope depletion patterns. Prograde formation of periclase was driven by infiltration of H$_2$O-rich fluid, with periclase forming at 620–710 °C. During retrograde cooling, fluids were also nearly pure H$_2$O, and brucite appeared at 570 °C followed by serpentine at 355 °C. Calculated volumes of fluid for the retrograde reactions require that infiltration of the wall rocks continued during cooling. If these findings can be extended to the Teakettle Junction aureole, it follows that the observed hydration front is a result of prolonged infiltration of H$_2$O-rich fluids during prograde and retrograde metamorphism. Proximity to the pluton contact and evidence for fluorine metasomatism suggest that the source of fluids was magmatic.

Though mentioned only briefly in this paper, plastic deformation of the country rocks occurs near the contact in the form of open to tight folds. This deformation is restricted to rocks inside the serpentine (forsterite) isograd, with an abrupt transition to strata that show only gentle regional folds. Kozak et al. (2004) also found that plastic deformation increased at the serpentine (forsterite) isograd in their study of the Ubehebe Peak aureole. Fluid infiltration and widespread hydration reactions within this zone, along with high temperature, may have facilitated plastic deformation. These findings suggest that in these aureoles, the serpentine (forsterite) isograd constitutes a fundamental discontinuity: closer to the intrusive contact, the chemical, physical, and mechanical effects of pluton emplacement increase significantly and become closely coupled.
examination of 64 thin sections with optical microscopy and SEM-EDS. This is especially noteworthy because with the exception of tremolite, most of the minerals mapped here are not easily identifiable on the basis of hand-lens inspection in the field, and many require SEM-EDS for identification. Detection limits for the OH- and F-bearing minerals in this study are estimated to be 1 vol% or less in most cases.

A key finding of this paper is that hydration of host rocks in the aureole is recorded both in the distribution of hydrous minerals and in the spatial variation in the overall depth of the OH absorption band near 1.4 μm. Significant hydration effects are limited to rocks inside the serpentine (forsterite) isograd; however, within that zone, hydration is variable at the outcrop scale. At greater distances from the contact, there is an abrupt decrease in the abundance of hydrous minerals and values of the OH band depth. The serpentine (forsterite) isograd is interpreted to represent a metamorphic hydration front.

Although the focus in this paper has been on advantages of Vis-NIR spectral studies, there are inherent limitations. In most cases, Vis-NIR spectroscopy by itself cannot determine the complete mineral assemblage, nor is it feasible to extract reliable estimates of absolute mineral proportions. Furthermore, the method does not provide information regarding textural relationships among minerals such as reaction or replacement textures. Though clearly not a substitute for conventional petrologic investigations, Vis-NIR spectroscopy can play an important and complementary role in mapping and in the overall characterization of metamorphic processes, and this method of spectroscopy has a unique role in linking field and laboratory studies to remotely sensed data.

APPENDIX. DETAILS OF ANALYTICAL METHODS

Field Spectrometers

To achieve maximum sensitivity across the 350-2500 nm (0.35-2.5 μm) wavelength range, the field spectrometers used in this study utilize three internal detectors, and the sampling interval and spectral resolution vary accordingly. In the case of the TerraSpec Halo that was used for most of the field measurements, the spectral sampling interval is ~1.4 nm in the wavelength range 350-1000 nm, and ~2 nm in the wavelength range 1900-2500 nm. Optimum spectral resolution is 3 nm at 700 nm, 9.8 nm at 1400 nm, and 8.1 nm at 2100 nm. Periodic checks of wavelength calibration using a Mylar standard indicated wavelength accuracy of ±1 nm, and long-term reproducibility measured on a nico schist sample with an absorption feature at 2201 nm is ±0.2 nm.

HyMap Airborne Imaging Spectrometer

HyMap airborne hyperspectral image data were acquired 9 June 2003 at ~17:30 UTC (10:30 local time). Acquisition included two overlapping flight lines, each ~25 km in length and 2300 m across track. Aircraft altitude was 2000 m, giving a ground sample distance (pixel size) of 5 m. The western three-quarters of the study area was covered by the HyMap acquisition. HyMap coverage and the area covered in Figure 3 are shown in Figure A1. The HyMap sensor covers the wavelength range 0.45-2.48 μm in 126 channels, with signal-to-noise ratio of 500-1000 (Cocks et al., 1998; Kruse et al., 2000). In the principal wavelength range used in this study (1.95-2.48 μm), the spectrometer resolution is 18-20 nm and the average sampling interval is 17 nm. Prior to flight, radiometric calibration was performed with Spectralon. In-flight calibrated radiance data were corrected for atmospheric absorption and converted to apparent reflectance using the HyCorr correction procedure, which uses radiative transfer modeling to remove atmospheric absorption effects. Specifically, HyCorr applies the ATREM3 (ATmosphere REMoval) code (Gao et al., 1993) followed by EFFORT (Empirical Flat Field Optimal Reflectance Transformation) polishing to smooth noisy features remaining after atmospheric correction (Boardman, 1998b). Geometric corrections and georeferencing are achieved through onboard differential GPS and inertial navigation systems.

HyMap Image Processing and Mineral Mapping

For each of the two HyMap flight lines, HyVista Corporation provided an apparent reflectance file and geometric lookup tables. These files were processed using ENVI software (Environment for Visualizing Images, L3Harris Geospatial Solutions). Each flight line was georectified to real-world coordinates, and the two lines were mosaicked into a single georeferenced image. For this study, a geographic subset centered on the Teakettle Junction aureole was extracted from the full mosaic.

The procedure for spectral mineral mapping followed the ENVI Spectral Hourglass Wizard (Kruse et al., 2000; Kozak et al., 2004; Kruse, 2007). Image spectra were post-processed to give a reduced set of noise-free spectral bands, and pixel spectral signatures were identified that corresponded to the key mineral end members. Identification of these image-derived end members was accomplished by comparison with published libraries of mineral spectra (Clark et al., 1993; Kokaly et al., 2017). Finally, maps showing the distribution of metamorphic minerals were generated from the image-derived spectral end members using the mixture tuned matched filtering (MTMF) algorithm (Boardman, 1998a). MTMF is a partial unmixing method for sub-pixel analysis that combines the strengths of matched filtered and linear mixture theory. For each end member, MTMF assigns to each pixel a matched filter score, which is a measure of the degree of match of the pixel spectrum to the reference end-member spectrum. MTMF also uses noise and image statistics to calculate an additional measure called infeasibility, which allows matched-filter false positives to be identified and rejected. Pixels with high matched-filter scores and low infeasibility for a given end member were considered to contain the mineral associated with that end member. Although matched-filter scores may be interpreted to indicate approximate sub-pixel abundance, results in Figure 7 show only that the end member is present in the pixel at a level that exceeds a user-defined threshold. In practice, thresholds were established such that spectra of the selected
1.283 Teakettle Junction and Ubehebe Peak aureoles. The reason for these features is ubiquitous, however, in spectra from the Clinohumite (Kozak et al., 2004) and other contact aureoles. Details specific to the minerals discussed in this study are included here.

Brucite

Vis-NIR spectra of brucite display numerous distinctive features (Table 1; Fig. 2), and the modal abundance of brucite is high in these samples, as it is at other locations with brucite marbles (Ferry and Rumble, 1997; Ferry et al., 2002). Spectral identification of brucite is considered very reliable. Diagnostic features in brucite spectra include the shape of the pattern between 2.160 μm and 2.318 μm and the feature at 1.299 μm.

Forsterite

As noted above, definitive identification of forsterite in Vis-NIR spectra is tenuous because it is based on a broad absorption feature (Table 1; Fig. 2). However, the shape and central wavelength of the broad absorption near 1.050 μm are consistent with Mg-rich olivine, and SEM-EDS results support the validity of the spectral interpretation presented here.

Serpentine

Serpentine has numerous sharp absorption features (Table 1; Fig. 2), and spectral identification of serpentine is considered very reliable. Diagnostic features in serpentine spectra include the pair of features at 2.109 μm and 2.130 μm and the feature at 2.128 μm. Distinct absorption features at 2.244 μm and 2.272 μm in Figure 2C are not characteristic of serpentine reference spectra (e.g., antigorite and chrysotile spectra in Clark et al. [1993]). These features are ubiquitous, however, in spectra from the Teakettle Junction and Ubehebe Peak aureoles. The reason for this difference is not clear. Unlike minerals in reference spectral databases, which are generally of high purity, samples in this study are rocks that contain minerals in addition to serpentine. Compositionally, SEM backscattered imaging and EDS element mapping indicate that some serpentine is a complex intergrowth of serpentinite along with additional phases that include Al and Mg hydroxides and minor Fe (Fig. 4A). It is possible that the presence of these phases affects the spectral characteristics of serpentinite.

Clinohumite

Vis-NIR reflectance spectra of humite-group minerals (norbergite, chondrodite, humite, clinohumite) are not included in standard reference databases such as Kokaly et al. (2017). Here, clinohumite identification is based on SEM-EDS verification and similarity to spectra of samples from the Birch Creek pluton, California, where fluorine metasomatism produced minerals of the humite group (Barton, 2000). Clinohumite spectra are characterized by diagnostic absorptions at 1.439 μm, 1.968 μm, and 2.303 μm (Table 1; Fig. 2).

Tremolite and Talc

Prominent absorption features in both tremolite and talc occur near 1.39 μm, 2.3 μm, and 2.39 μm (Table 1; Fig. 2), but these show significant overlap (Laukamp et al., 2012). These three regions also are affected by interference from carbonates and other hydrous Mg-silicates (Fig. 2C). For this study, tremolite and talc identification focused on secondary features near 2.111 μm and 2.077 μm, which are diagnostic of tremolite and talc, respectively. Pure talc has additional absorption features near 1.53 μm and 2.01 μm that could be used to differentiate it from tremolite, but these features were not reliably detected because of the very low modal abundance of talc in the samples. Note that in Figure 2 the tremolite spectrum is from a sample that is relatively pure, so the 2.111 μm feature is distinct, whereas the talc spectrum is from a sample for which the SEM-EDS estimate of talc abundance is 1 vol%, so the 2.077 μm feature is imperceptible at the vertical scale in the figure. Because these features are generally small and the modal abundances are low, the identification of tremolite and talc is considered to be less certain than that of other minerals discussed here.

Phlogopite and Ilite

Pure phlogopite has absorption bands near 2.245 μm and 2.376 μm, but these overlap with features of several other minerals (Table 1; Fig. 2C). However, the band at 1.377 μm is relatively free from overlaps and is considered diagnostic of phlogopite. This band is evident in Figure 2B in the spectra for phlogopite, forsterite, and dolomite, and it forms a minor shoulder in the spectrum for calcite and possibly the spectrum for serpentine. Minerals of the illite-muscovite series have an absorption feature near 2.111 μm that is distinctive among the minerals in this study (Table 1; Fig. 2B) as well as a band near 2.210 μm that commonly forms a left shoulder on the broader dolomite 2.318 μm feature (Fig. 2C).

Dolomite and Calcite

The principal absorption bands for dolomite and calcite occur at 2.318 μm and 2.338 μm, respectively (Table 1; Fig. 2C). In samples with a mixture of these minerals, the wavelength of this band occurs at intermediate values. In relatively pure samples, dolomite and calcite can also be identified on the basis of minor bands between 1.856 μm and 2.154 μm (Fig. 2A); however, these bands were not always evident in samples in this study.

ACKNOWLEDGMENTS

Preliminary work on this project was supported by U.S. National Science Foundation grant EAR-9708629. P.K. Kozak assisted in the field, and M. Cochran-Bjerke, M.M. Day, and C.V. Price assisted with geospatial analysis. The cooperation of the U.S. National Park Service, Death Valley National Park, is gratefully acknowledged (research permit DEVA-00205). The author acknowledges constructive reviews by B.L. Ehlmann, Associate Editor M.L. Williams, S.R. Beeler, and an anonymous reviewer.

REFERENCES CITED

Adams, J.B., 1974, Visible and near-infrared diffuse reflectance spectra of pyroxenes as applied to remote sensing of solid objects in the solar system: Journal of Geophysical Research, v. 79, p. 4829-4836, https://doi.org/10.1029/JB079i032p04829.

Barton, M.D., 2000, Overview of the lithophile element-bearing magmatic-hydrothermal system at Birch Creek, White Mountains, California, in Dilles, J.H., Barton, M.D., Johnson, D.A., Proffett, J.M., Einaudi, M.T., and Crafford, E.J., eds., Part I: Contrasting Styles of Intrusion-Associated Hydrothermal Systems: Society of Economic Geologists Guidebook 32, p. 9-26.

Boardman, J.W., 1986a, Leveraging the high dimensionality of AVIRIS data for improved sub-pixel target unmixing and rejection of false positives: Mixture tuned matched filtering, in Green, R.O., ed., Summaries of the Seventh JPL Airborne Earth Science Workshop, January 12–16, 1986: Volume 1. AVIRIS Workshop: Jet Propulsion Laboratory Publication 97-21, v. 1, p. 55.

Boardman, J.W., 1986b, Post-ATREM polishing of AVIRIS apparent reflectance data using EFFORT: A lesson in accuracy versus precision, in Green, R.O., ed., Summaries of the Seventh JPL Airborne Earth Science Workshop, January 12–16, 1998: Volume 1. AVIRIS Workshop: Jet Propulsion Laboratory Publication 97-21, v. 1, p. 55.

Burchfiel, B.C., 1969, Geology of the Dry Mountain quadrangle, Inyo County, California: California Division of Mines and Geology Special Report 99, 19 p.

Clark, R.N., 1989, Spectroscopy of rocks and minerals and principles of spectroscopy, in Renz, A.N., and Ryerson, R.A., eds., Manual of Remote Sensing: Volume 3. Remote Sensing for the Earth Sciences (third edition): New York, Wiley, p. 3-58.

Clark, R.N., and Roush, T.L., 1984, Reflectance spectroscopy: Quantitative analysis techniques for remote sensing applications: Journal of Geophysical Research, v. 89, p. 6329-6340, https://doi.org/10.1029/JB089iB08p06329.

Clark, R.N., King, T.V., Kleiwa, M., Swayze, G.A., and Vergo, N., 1990, High spectral resolution reflectance spectroscopy of minerals: Journal of Geophysical Research, v. 95, p. 12,653–12,680, https://doi.org/10.1029/JB095iB08p12653.

Clark, R.N., Swayze, G.A., Gallagher, A.J., King, T.V., and Calvin, W.M., 1993, The U.S. Geological Survey, Digital Spectral Library: Version 1: 0.2 to 3.0 μm: U.S. Geological Survey Open File Report 93-592, 1340 p., https://doi.org/10.3133/ofr93592.

Cocks, T., Jenssen, R., Stewart, A., Wilson, I., and Shields, T., 1998, The HYMap airborne hyperspectral sensor: The system, calibration and performance, in Schaeppman, M., Schläfer, D., and Itten, K.I., eds., Proceedings of the First EARSeL Workshop on Imaging Spectroscopy: Zurich, Remote Sensing Laboratories, University of Zurich, p. 37-42.

Cook, S.J., and Bowman, J.R., 2000, Mineralogical evidence for fluid-rock interaction accompanying prograde contact metamorphism of silicic domolites: Alta stock aureole,
