

Spectroscopic study of the Moses Lake dune field, Washington: Determination of compositional distributions and source lithologies

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[1] Source lithologies and transport histories of materials within the Ephrata Fan are investigated. Data were collected using a variety of remote-sensing, laboratory spectroscopic, and field observations and techniques. Laboratory thermal emission spectra were collected of bedrock within the Grand Coulee, dune samples, and clast deposits. Factor analysis, target transformation, and end-member recovery techniques were applied to the set of dune samples as well as a set of grain size fractions. The dune sample spectra are composed of three components that represent basalt, granodiorite, and clay compositions. The basalt and granodiorite components are similar to spectra of clast and bedrock samples from the Grand Coulee and the Ephrata Fan. The clay component is similar to weathering surfaces located within the dune field. The same components were recovered from the set of grain size fractions from a single dune sample demonstrating a relatively higher basalt concentration with grain sizes greater than $\sim 250 \mu\text{m}$. Thermal Infrared Multispectral Scanner (TIMS) data display significant intradune compositional variation and no discernable interdune compositional variation, indicating that the basalt and granodiorite components were likely deposited simultaneously and subsequently separated by wind based on grain size. Basalt and granodiorite bedrock units within the Channeled Scablands are source materials for the deposits within the Ephrata Fan and Moses Lake dune field. The Columbia River, located 20 km west of the dune field, is not a likely source of material. *INDEX TERMS*: 5410 Planetology: Solid Surface Planets: Composition; 5464 Planetology: Solid Surface Planets: Remote sensing; 5470 Planetology: Solid Surface Planets: Surface materials and properties; 5494 Planetology: Solid Surface Planets: Instruments and techniques; 6207 Planetology: Solar System Objects: Comparative planetology; *KEYWORDS*: Infrared spectroscopy, factor analysis, outflow channels, sediment transport

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1. Introduction

[2] Martian eolian dunes and catastrophic flood deposits are considered to be useful tools from which geologic histories and Martian lithologic properties may be discerned via orbital and in situ remote sensing. For example, in 1997 the Mars Pathfinder spacecraft landed on a plain covered by flood deposits from Ares and Tiu Valles with the intent to learn something about the composition of the cratered highland rock through which these valleys are cut [Golombek *et al.*, 1997, 1999]. Likewise, from orbit, sand dunes offer relatively dust-free surfaces composed of grains typ-

ically 100–500 μm in size [Edgett and Christensen, 1991] that can be observed via multispectral infrared instruments to determine mineral or lithologic composition [e.g., Blount *et al.*, 1990; Ramsey *et al.*, 1999; Edgett, 1994a]. Indications from the Thermal Emission Spectrometer (TES) aboard Mars Global Surveyor (MGS), for example, suggest that dunes in the Martian north polar region have a composition that is more silicic than those in the southern highlands—those in the north can be considered as andesitic, while those in the south can be classified as basaltic [Bandfield *et al.*, 2000a; Christensen *et al.*, 2000a, 2000b].

[3] The MGS TES has been in orbit around Mars since September 1997 and is expected to continue to collect high spectral resolution observations in the 200–1650 cm^{-1} (6 to 50 μm) range through at least April 2002. A second orbiter,

2001 Mars Odyssey, carrying the 9-channel Thermal Emission Spectral Imager (THEMIS) finished aerobraking at Mars in January 2002. In 2003, the Mars Exploration Rovers (MER) will be sent toward Mars, each carrying a miniTES to obtain spectra of rocks and regolith from a vantage point near the surface. With these thermal infrared experiments in mind, particularly the MGS TES and Odyssey THEMIS, a terrestrial eolian dune field was sought in 1990 as a potential test bed for validating algorithms and approaches to analysis of thermal infrared spectra from Mars.

[4] Prior to the MGS mission, all ground-based and orbiter-based evidence suggested that Martian dunes would be mafic rather silicic like their quartz-rich counterparts on Earth (see discussion by *Edgett and Lancaster* [1993]). The largest known basaltic dune field on Earth is located in the Moses Lake, Washington, area in western North America. Petrographic analysis by *Petrone* [1970] suggested that the dune sand at Moses Lake is a mixture composed mainly of basalt lithic fragments and quartz grains. These two very different materials were considered to form a simple two-component mixture that could be used to begin to test some of the spectral analysis techniques that were being developed during the 1990s for application to Mars thermal infrared data.

[5] This paper is an initial analysis of Moses Lake dune sand in the context of using thermal infrared spectra and remote-sensing observations. These data are applied to the testing of a specific, focused hypothesis. In his thesis, *Petrone* [1970] concluded that there are two sources for the sand comprising the Moses Lake dunes: 1) in situ reworking and subsequent downwind transport of basaltic sand originally deposited by the catastrophic Spokane or Scabland floods, and 2) windblown transport to the basaltic dune field of ~95% quartz sand from the Columbia River bed located in a gorge roughly 20 km from the nearest present-day dune field. This study tests *Petrone's* conclusion regarding a Columbia River source, and finds 1) that the windblown sands in the adjacent Columbia River gorge are not as quartz-rich as *Petrone* had concluded, and 2) that the types and abundances of materials comprising the Moses Lake Dunes are more consistent with an origin entirely by eolian reworking of Scabland flood sediment transported and in large part derived from within the Grand Coulee channel located approximately 30 km north of the dune field.

[6] *Ramsey et al.* [1999] has shown the ability of thermal infrared remote-sensing data to greatly facilitate the determination of spatial distributions and sources of mineralogical eolian units. Previous work is expanded upon here by demonstrating the ability to interpret a more complex spatial distribution of mineralogical composition that does not demonstrate a clear geographical relation to any source. In addition, the spectral signature of mineralogical units that are independently variable, but are mixed at the scale of the spectral measurement, may be isolated without physically separating the sample. This ability to isolate compositional units is important with remotely sensed data where spatial sampling is on the order of meters to kilometers, as well as laboratory data where separation of mineralogical units may be inaccurate as well as tedious and time-consuming as in the case of a mixed sand.

[7] The combination of in situ field observations, remote-sensing data, and laboratory measurements are complimen-

tary methods that allow for a much clearer interpretation of a scientific problem than any of these methods would individually. The TIMS data used in this study is excellent for distinguishing compositional units and providing their spatial distribution over large areas that might not be easily sampled or accessed [*Kahle*, 1987; *Gillespie*, 1992; *Weitz and Farr*, 1992; *Hook et al.*, 1994; *Crowley and Hook*, 1996; *Ramsey et al.*, 1999; *Ramsey and Fink*, 1999]. In situ field observations provide textural and relational observations in addition to adding confidence to both remote-sensing and laboratory data interpretations. The laboratory measurements provide quantitative compositional information that cannot be achieved through either visual analysis or the limited spatial and spectral resolution of the remote-sensing data sets.

2. Geologic and Temporal Setting

[8] The Moses Lake dune field is located in the southern Quincy Basin of central Washington state, largely south and west of Moses Lake, north of the Frenchmen Hills, and south of U.S. Interstate Highway 90 (Figure 1). The Quincy Basin is a structurally controlled depression formed within the Tertiary Yakima Basalt Subgroup of the Columbia River Basalt Group. Much of the basaltic dune sand is considered to have been reworked from sediment deposited in the Quincy Basin during one or more of the multiple Lake Missoula or Channeled Scabland flood events that swept across eastern Washington and the underlying Columbia Basalts between 17,000 and 12,000 years ago [*Bretz et al.*, 1956; *Nummedal*, 1978]. These multiple flood events, caused by the catastrophic breaching of an ice dam at Lake Missoula, created a landscape that is known today as the Channeled Scabland, the biggest channel of which is the Grand Coulee that runs several hundred kilometers from northeastern Washington to the Ephrata Fan in northern Quincy Basin. *Bretz* [1969] proposed that there were at least eight separate flood events, others have suggested that there were as many as 40 to 100 events [see *Baker and Bunker*, 1985; *Waite et al.*, 1994]. The dunes (Figure 2) are located at the distal end of the Ephrata Fan, a broad expanse of boulders, cobbles, and gravel deposited by one or more of the Missoula Floods [*Bretz et al.*, 1956; *Rice and Edgett*, 1997]. The Ephrata Fan begins just south of Soap Lake at the southern end of the Grand Coulee (Figure 1). Water from the Scabland floods poured through a narrow constriction point and then expanded out into the Quincy Basin, forming the fan-shaped deposit. Boulders up to 18 m in size are found near and just south of this constriction point [*Bretz et al.*, 1956; *Edgett et al.*, 1995, pp. 46–48], but the deposit fines southward into gravels, and, at Moses Lake, sand. The clasts that make up the Ephrata Fan, at least at the surface, are dominated by basalt lithics with lesser amounts of granodiorite [*Gulick*, 1990; *Rice and Edgett*, 1995], both of which outcrop within the Grand Coulee (the granodiorite lies beneath the basalts). Several images of the coulee, clasts, and dunes are shown in Figure 3.

[9] The climate in the Quincy Basin area has been arid and semi-arid since the Missoula floods, as documented in two studies of the post-Missoula dune field 40 km south of the Moses Lake dunes on the Hanford Nuclear Reservation [*Smith*, 1992; *Stetler*, 1993]. Late Pleistocene and Holocene winds have driven the Moses Lake sands east-northeast-

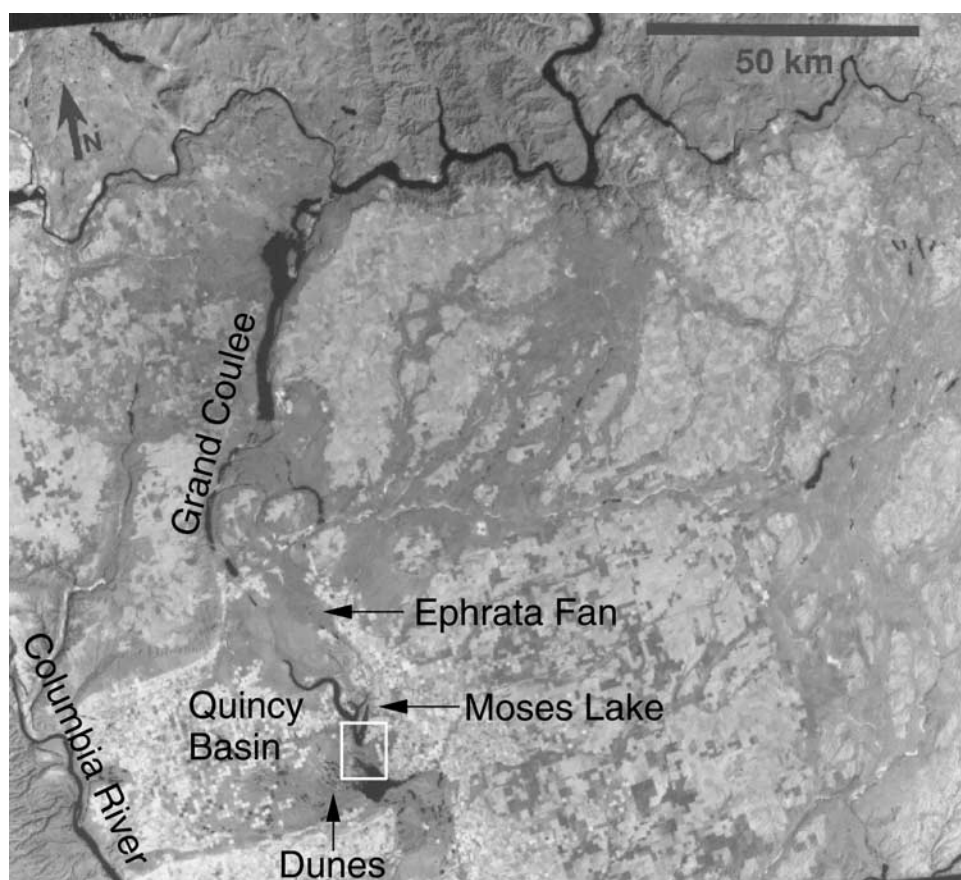


Figure 1. Regional view of the Quincy Basin and Grand Coulee in central Washington. The image is from the Landsat spacecraft taken on 29 September 1992. The white box indicates coverage of Figure 2 on the image. Center near $47^{\circ}27'N$, $118^{\circ}49'W$.

ward. Today, much of the Moses Lake dune field occurs stratigraphically above the gravels and cobbles of the central and eastern portions of the distal Ephrata Fan, which in turn lies above a scabland of eroded Wanapum Basalt units [Grolier and Bingham, 1971; Gulick, 1990]. The eastward advance of the dunes eventually dammed a portion of Rocky Ford Creek to create Moses Lake.

[10] The dunes from a distance on a sunny day appear to be brown to blue-black in color; hand samples are nearly black with minor amounts of lighter-toned or white grains. Petrone [1970] found the sands to generally consist of more than 55% basalt lithic fragments; lighter-toned grains comprising most of the remaining bulk were interpreted as quartz on the basis of binocular microscope analysis. Other lithic fragments cover a range of compositions including small pieces of schists transported first by glaciers then by Missoula Floods from somewhere on the Canadian Shield. The Moses Lake dune field might be the largest basaltic eolian sand accumulation on Earth [Edgett and Lancaster, 1993].

[11] Using the terminology of McKee [1979], the dunes include parabolic and crescentic forms which are active today. The dunes' rate of advance is thought to have been significantly slowed during the past century—on the basis of eyewitness anecdotes, multiyear aerial photograph analysis, and dune positions in 1992 relative to Mount St. Helens tephra deposits from 1980 on interdune surfaces [Petrone, 1970; Edgett, 1994b].

[12] With the Columbia Basin Project, the Moses Lake dune field became subject to a rising water table [Walters and Grolier, 1960, p. 16] and creation of wetlands on 29 May 1952, when the first irrigation water from the Grand Coulee arrived in the dry ditches near Moses Lake [Holbrook, 1956, p. 318]. The O'Sullivan Dam was emplaced in 1952, forming a catchment for irrigation runoff that flooded a large fraction of the dune field and created the Potholes Reservoir. Dunes west of the reservoir became much more wet and vegetated, although some fraction of each of the larger dunes remained subject to further downwind movement. Dunes east of the reservoir remained largely unvegetated because of their higher elevation above the water table, but the supply of sand from the west was diminished and local farmers attempted to stabilize the dune field with bales of hay and planted grasses [Petrone, 1970]. Dune activity was further affected by the 18 May 1980 explosive eruption of Mount St. Helens. The region including the Moses Lake dune field received some of the thickest (2–3 cm) deposits of silt- and clay-sized tephra [Sarna-Wojcicki et al., 1980]. While most dunes eventually lost their covering of tephra, some smaller dunes and dune ridges have remained covered and developed a crusted surface that persisted well into the 1990s [Edgett, 1994b]. Larger dunes continued to advance at an estimated ~ 3 m/year based upon field observations in 1992 and 1998 based on measurements of dune slip

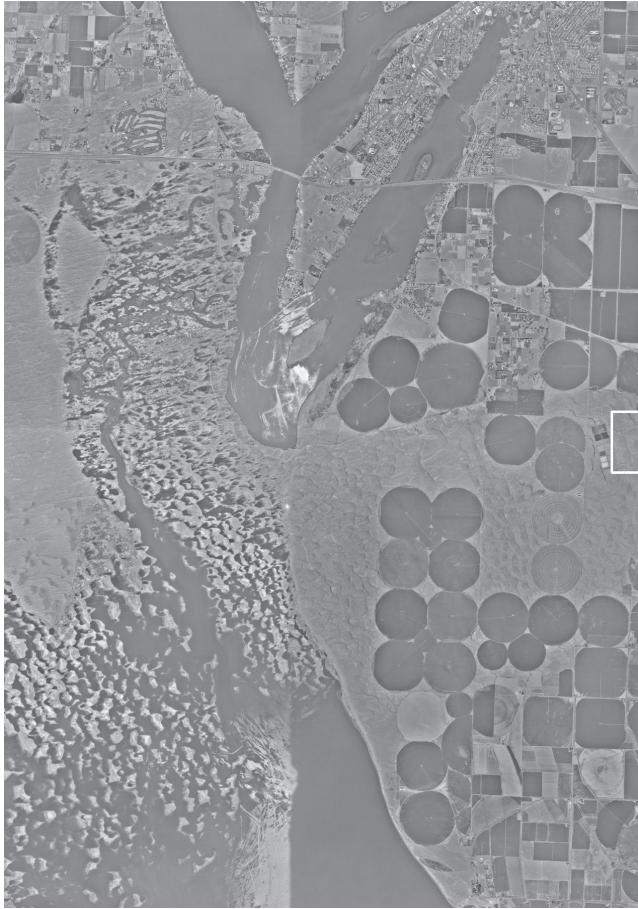


Figure 2. Aerial photograph of the Moses Lake Dunes. The Potholes Reservoir has flooded much of the dune field in the lower left portion of the image, creating islands out of individual dunes. The dune field itself naturally dams Moses Lake at the upper part portion of the image. The white box indicates coverage of Figure 13 on the image. Images are USGS digital orthophotos taken 8 and 13 July 1996, Moses Lake South, NW, NE, SW, and SE. Circular fields have a diameter of $\sim 2/3$ km.

faces relative to a 6-cm-thick layer of 1980 tephra preserved and visible within the location of the 1980 slip face [Edgett, 1994b].

[13] Dune activity at Moses Lake was further affected in the 1980s and 1990s by additional changes in land use. Most of the dune field south and west of Moses Lake and the Potholes Reservoir is now a wetland and wildlife preserve. The dunes occurring east of the Potholes Reservoir have been subject to other, human-induced effects that generally stabilized or destroyed the dunes. However, a small portion of the dune field between northeastern Potholes Reservoir and southern Moses Lake is reserved for recreational vehicle traffic. This area remains the most geologically active portion of the dune field because the vehicles prevent vegetation from growing.

3. Approach

[14] Several data sets and analysis techniques were used to both gain an understanding of the processes in effect in

the Ephrata Fan and evaluate the effectiveness of the techniques themselves. Remote-sensing data collected includes simultaneously collected air photos and TIMS imaging data that cover much of the dune field and extend to the Columbia River to the west. A hardcopy Landsat scene of the entire Ephrata Fan area was also acquired. Samples of dune sand, clast deposits, and bedrock were also

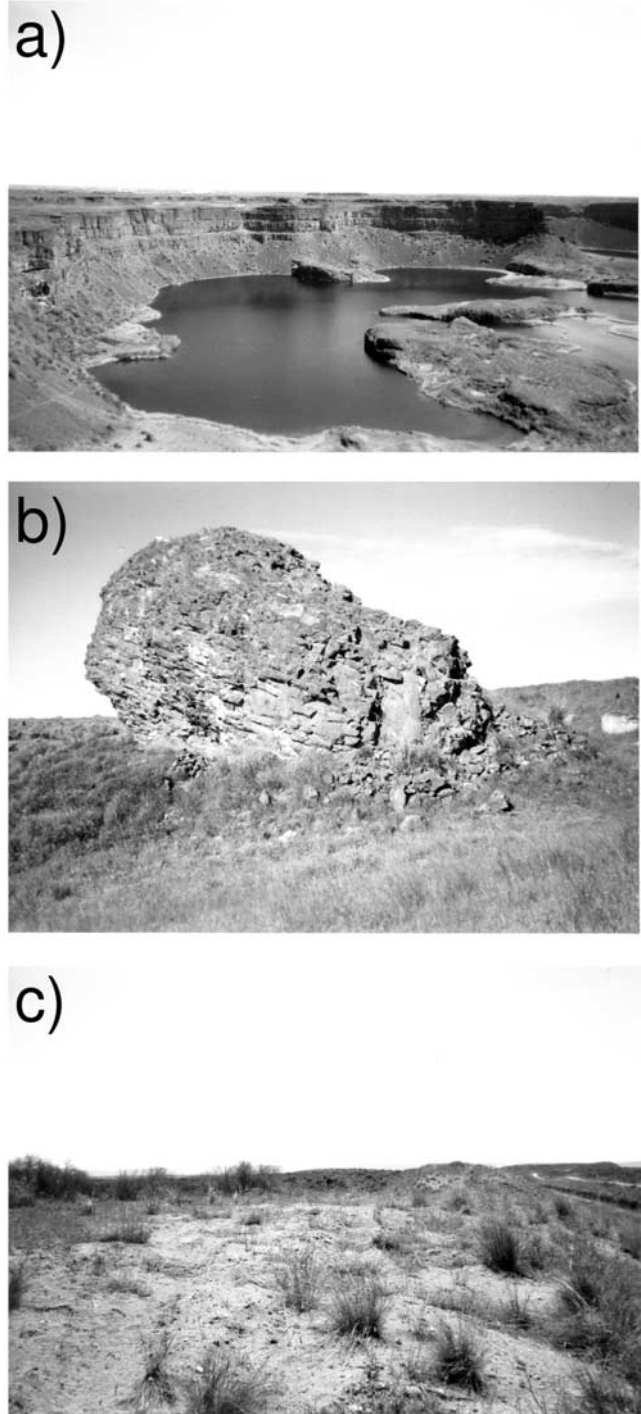


Figure 3. Field photographs of (a) Grand Coulee (~ 0.5 km across), (b) clasts on the Ephrata Fan (boulder is ~ 8 m high), and (c) Moses Lake dune field (plants in foreground are ~ 0.5 – 1.0 m tall).

collected as well as field observations. Thermal emission spectra of the collected samples were obtained in the laboratory.

[15] A variety of techniques were used to evaluate the data sets. Observations were made in the field, of hand samples, and air photos to provide a visual inspection of the area and a qualitative determination of composition and texture of samples. The TIMS data were processed using a standard decorrelation stretch in order to visually enhance surface compositional variations [Gillespie *et al.*, 1986]. The laboratory spectra were evaluated using qualitative comparisons, factor analysis and end-member recovery [Bandfield *et al.*, 2000b], and deconvolution techniques [Ramsey and Christensen, 1998; Ramsey *et al.*, 1999].

[16] TIMS data were acquired on 13 July 1992 (site 9224, lines 1–4) at $\sim 4\text{m}/\text{pixel}$ resolution of the entire dune field. Because no atmospheric information was obtained simultaneously with the TIMS data, a standard midlatitude summer atmospheric model was used with MODTRAN [Berke *et al.*, 1989] to provide an atmospheric correction. A decorrelation stretch image using TIMS bands 5, 3, and 1 projected as red, green, and blue respectively was produced similar to that of Ramsey *et al.* [1999]. A subset of the image that contained only the dune field was used to provide the rotation and stretch for the entire data set. This was done in order to maximize the contrast within the dune field rather than the farmland, volcanic ash, and water that form the majority of the TIMS data set but are not the focus of this study.

[17] Initial field reconnaissance and sample collection was conducted by K.S.E. from 30 September through 6 October 1990. This was followed by a more extensive field sampling by K.S.E. 19–27 August 1992. The 1992 goal was to sample a large number of dunes over the entire dune field. Samples from 14 different dunes were collected in 1990, and 50 individual dunes were sampled in 1992.

[18] Samples were taken by scraping grains from the upper 2–5 mm of the surface over an area approximately 0.5 by 0.5 m and placing them in sealed, airtight plastic bags for transport back to the laboratory. For uniformity, samples from the crest of each dune sampled were collected in this manner. For several dunes, additional samples were collected at various places on the stoss and slip face slopes (again, upper 2–5 mm over 0.5 m area).

[19] A second set of field observations and samples were acquired by J.L.B. during April of 1998. The focus of this second sample collection was of larger clast size samples in the Ephrata Fan, bedrock samples from the Grand Coulee, and dune samples from the Columbia River. Each of these areas was investigated as possible sources of the dune material and samples were taken for laboratory spectral acquisition. Dune samples were collected from the top 5 mm of the surface and rock samples were broken in order to retrieve both a fresh and weathered surface on each sample.

[20] Laboratory spectra were acquired and calibrated using the method 1 of Christensen and Harrison [1993] as modified by Ruff *et al.* [1997] using a Mattson Cygnus spectrometer equipped with a KBr beamsplitter and a DTGS detector. Spectra were obtained between $2000\text{--}400\text{ cm}^{-1}$ ($5\text{--}25\text{ }\mu\text{m}$) at a sampling interval of 2 cm^{-1} . Dune samples were poured into a $\sim 3\text{ cm}$ diameter and 0.5 cm deep copper cup which was actively heated to a temperature of 80 C

during spectral acquisition. Hand samples were heated to 80 C and are not actively heated during spectral acquisition. 180 scans were acquired of each sample over a ~ 5 minute period and averaged to improve the signal-to-noise ratio. Ruff *et al.* [1997] extensively analyzed possible sources of error in this technique and determined a precision of better than 1% emissivity and accuracy of better than 2% absolute emissivity.

[21] Because the hand samples were constantly cooling during spectral acquisition there was some concern of possible effects introduced in the spectra due to the anisothermality. To verify that this was not a significant effect introduced in the spectra, three spectra were acquired using only 60 scans each over a ~ 5 minute period. These spectra were averaged before calibration to simulate the standard 180 scan spectral acquisition procedure as well as individually calibrated in order to significantly reduce the amount of temperature change during spectral acquisition. The result verified that the sample temperature change during acquisition of the spectra does not have a significant effect on the calibrated spectra.

[22] Spectra of samples taken from the top 2–5 mm of the crest of 39 dunes covering the extent of the dune field as well as a set of 6 grain size fractions were run separately through a spectral factor analysis and end-member recovery technique described by Bandfield *et al.* [2000b] and summarized below. This is a combination technique that uses factor analysis (R-mode, mean removed) and target transformation as adapted from Malinowski [1991] used as a spectral end-member recovery technique that allows for isolation of spectral end-members from a set of mixed data [Bandfield *et al.*, 2000b]. Factor analysis provides an indication of the complexity of the data set, including the number of independent end-member components within a data set. The end-member recovery technique provides the ability to recover the spectral shape of end-members from a set of mixed spectra even if the exact end-member is not present in a set of reference spectra.

[23] Factor analysis derives the eigenvalues and eigenvectors from the set of mixed spectra to determine the number of components that influence the system. The eigenvalues that correspond to each of the derived eigenvectors describe the amount of variance contributed to the system along the axis parallel to the eigenvector. The value of this analysis is the reduction of multidimensional data into just a few dimensions. For example, if there are only three components varying within a system, the system can be reconstructed within the limits of the noise present with linear combinations of the first three eigenvectors.

[24] The maximum dimensionality that can be spanned by the spectra is the number of spectral end-members. Because the number of spectral bands in the laboratory data (usually $>100\text{s}$) greatly exceeds the number of significant end-member components (typically less than 5), the spectra will lie in a space contained within the higher dimensionality of the data set with a number of dimensions equal to the number of end-members. As the derived eigenvalues and eigenvectors account for any variation as efficiently as possible, the first n eigenvectors, where n is the number of spectral end-members present, will span this space that is also spanned by the data [Malinowski, 1991]. This indicates that all the data and the spectral end-members

may be reconstructed by linear combinations of these first eigenvectors.

[25] Target transformation is a test for the fit of a possible spectral end-member to the set of mixed spectra. If the possible end-member, called the trial spectrum, is a spectral end-member, then the trial spectrum is contained within the space spanned by the significant eigenvectors. As a result, the trial spectrum may be reconstructed as a linear combination of the significant eigenvectors. To determine whether or not a trial spectrum is contained within the eigenvector space, a combination of eigenvectors are fit to the test spectrum in a least squares manner and the test and eigenvector combination, called the best fit spectrum, are compared to determine their similarity. The target transformation is performed on each trial spectrum separately, which allows the determination of individual end-members independent of the determination of others [Malinowski, 1991; Bandfield et al., 2000b].

[26] Inspection of the best fit spectra from the target transformation for numerous test cases show that even for many failed transformations, where the best fit and trial spectra are not similar, the best fit spectrum is an accurate spectral end-member [Bandfield et al., 2000b]. For successful target transformation trials, the best fit spectrum is a refined and more accurate end-member than the trial spectrum. The end-member recovery technique takes advantage of this property in the analysis of a data set by allowing for the recovery, in addition to confirmation, of the set of true spectral end-members for the system from a group of best fit spectra that result from the target transformation. There is no automatic system for this selection and both human experience and bias are introduced with the selection of these end-members. However, as discussed below, the validity of this selection may be checked. These recovered end-members may be analyzed further for their properties and mineralogical compositions.

[27] Obtaining a spectral end-member using a trial spectrum that is not necessarily similar to the best fit spectrum is demonstrated in Bandfield et al. [2000b]. Because the target transformation is simply fitting the trial spectrum with a linear combination of eigenvectors in a least squares manner, there is no uniqueness of one combination over another. Spectral shapes of substances are broadly similar to each other, however, and the trial spectra produce realistic spectral shapes from the eigenvectors even if the specific spectral end-member is not present in the set of trial spectra. Because end-members show a greater spectral contrast than mixtures (i.e. features are more pronounced), the target transformation method is practical for obtaining the end-members present in a system. The target transformation matches as well as possible the relatively high spectral contrast present in the trial spectrum by fitting a combination of the eigenvectors to the trial. As a result, best fit spectra are often spectral end-members. Spectral end-members are generally recovered with trial spectra that contain absorptions near the same wavelengths as the spectral end-members, but these absorptions are not necessarily the same shape.

[28] The ability to obtain end-members through the best fit spectra does necessitate the use of a spectral library, but end-members present in the library need only be broadly similar in band position and shape to those in the data.

Small variations in features are recovered in the best fit spectra. If the spectral end-member is not present in the trial set, it may be recovered in the best fit spectrum of a trial spectrum that is only approximately similar in shape to the end-member [Bandfield et al., 2000b].

[29] It has been shown that the thermal infrared spectrum of a mixed surface may be closely modeled using a linear combination of the end-member spectra weighted by the aerial concentration of each end-member [Adams et al., 1986; Thomson and Salisbury, 1993; Ramsey and Christensen, 1998; Ramsey et al., 1999]. The deconvolution provides a linear least squares fit of the measured spectra using combinations of the recovered end-member spectra and the weightings represent the component abundances [Ramsey and Christensen, 1998]. It also provides an independent check on the validity of the selected spectral end-members. If the selected end-members are correct, then the component sums will be unity, RMS error between the measured and modeled spectra will be approximately equal to the RMS noise level of the spectra, and the component percentages will be between 0 and 100%. An additional check on the validity of the spectral end-members is to verify their linear independence. This check is done by confirming that no selected end-member can be modeled as a linear combination of the other end-members selected.

[30] The recovered end-members from the dune sample sets were compared to spectra of samples taken from larger clasts, bedrock, and dunes near the Columbia River to determine their mineralogical similarity. The TIMS data and in situ observations were used to identify possible sources and spatial distributions of these materials.

4. Results

4.1. Introduction

[31] The focus of the analysis is on the components, composition, and spatial distribution of the bedrock, clasts, and sand in order to determine the sources and distributions of the materials deposited on the Ephrata Fan. The results will be separated into observations and spectral characteristics of the bedrock units and large clasts followed by a spectral analysis of the dune samples. The spatial distribution of the source materials for the dunes is shown using the processed TIMS image in addition to analysis of the spatial distribution of spectral characteristics of the dune samples using the laboratory spectra.

4.2. Bedrock Lithology

[32] Bedrock units are visible toward the north and northeast in the walls of large channels cut by the floods. The largest of these channels, the Grand Coulee, was inspected and sampled for possible source materials that are distributed throughout the Ephrata Fan. The mouth of the channel lies ~30 km north of the dune field. The walls of the channel consist of massive to vesicular basaltic layers from lava flows. These walls consist of the Wanapum and Grande Ronde units of the Columbia River Basalt Group that is regionally widespread and is the only compositional bedrock unit visible in the area within ~60 km north (upstream) of the channel opening [Stoffel et al., 1991].

[33] Farther up the channel, the bedrock type transitions from basalt to an underlying granodiorite unit. The miner-

alogy of the granodiorite unit is dominated by a predominance of biotite, quartz, and plagioclase that has a 'salt and pepper' texture and appearance. Other textures and compositions within the granodiorite unit are present as well including a gneissic texture that concentrates the biotite in bands and local areas with a much increased potassium feldspar content with crystals of up to ~ 3 cm in diameter. No other bedrock types are present within the Grand Coulee to the Coulee Dam, ~ 75 km north of the channel mouth, with the exception of minor outcrops of Oligocene meta-sediments ~ 100 km up the channel [Stoffel *et al.*, 1991].

4.3. Large Clasts

[34] Several sites within the Ephrata Fan between the mouth of the Grand Coulee and the dune field were inspected and sampled to obtain the distribution and composition of the larger clasts (pebble to boulder sized) interpreted to be deposited by the floods. These observations found only granodiorite and basalt clasts to be present. The clasts are similar in appearance and composition to the two major bedrock units present within the Grand Coulee. Most clasts are well rounded and weathered. These weathering surfaces give the granodiorite clasts a dark color comparable to the basalt clasts.

[35] The size distributions of the two clast types are noticeably different. Basaltic clasts are common in a size range between several centimeters to several meters in diameter and were seen up to ~ 10 m in diameter. The granodioritic clasts are commonly ~ 1 to several meters in diameter, though several smaller clasts were found. Visual estimates at the sites examined place the concentration of granodioritic clasts >1 m in diameter at $\sim 25\%$ and the percentage <1 m in diameter at $<1\%$. Basaltic clast size generally decreases with distance from the channel mouth, though there are localized concentrations due to the formation of bars by the floods. However, no large concentration of granodioritic clasts <1 m in diameter was found. The reason for the differences in clast size distributions between the basalt and granodiorite compositions is unclear.

4.4. Spectral Characteristics of Clasts and Bedrock

[36] The spectral characteristics of the fresh surfaces of both the granodiorite and basalt compare well with samples of similar mineralogy analyzed by Feely and Christensen [1999] (Figure 4). The granodiorite samples show the characteristic silicate absorptions dominated by quartz at short wavelengths between 1000 – 1200 cm^{-1} as well as several narrow absorptions at >550 cm^{-1} . The basaltic samples have the typical relatively featureless bowl shaped absorption between 800 – 1100 cm^{-1} as well as 500 cm^{-1} . Both of these compositions are identifiable by their spectra and are consistent with the visual analysis.

[37] Weathering products and coatings are present on many of the rock samples. These are most prevalent on the clast samples that have been resting in soils that may retain moisture much longer than bedrock outcrops. In some cases, these weathered or coated surfaces may completely obscure the spectral signature of the rock (Figure 5). The spectral signature of these surfaces have a narrow absorption between 1000 – 1100 cm^{-1} characteristic of clay minerals such as iron smectite or montmorillonite [Christensen *et al.*, 2000c].

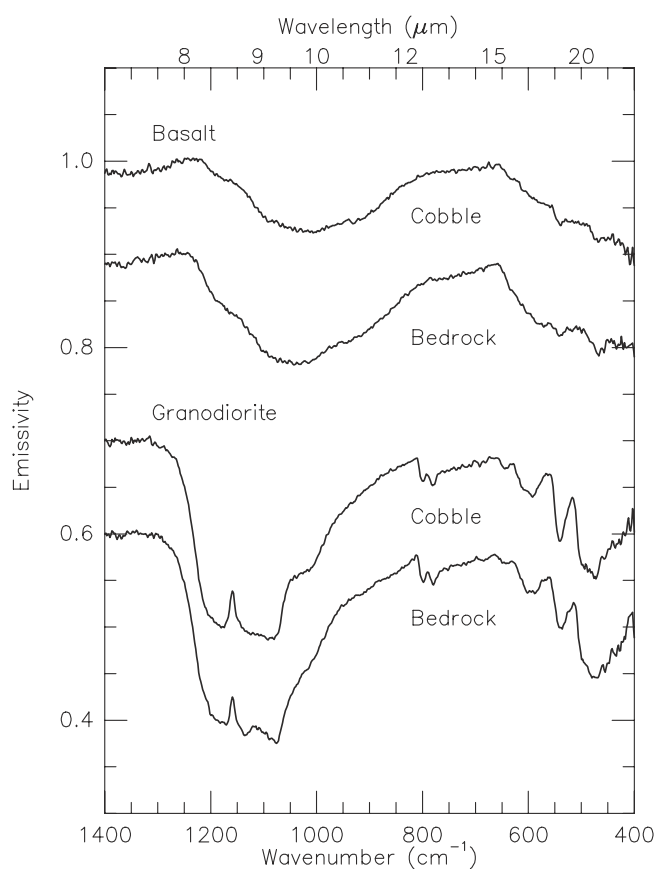


Figure 4. Basalt and granodiorite clast and bedrock sample spectra. Spectra were acquired from fresh surfaces of all samples. In both cases, the overall spectral signatures are similar indicating similar mineralogical compositions of both clasts and bedrock.

4.5. Columbia River Sands

[38] An additional possible source material to consider for the Moses Lake dune field is sand from the Columbia River. There are several small dune fields immediately east of the Columbia River that appear to be migrating east toward the Moses Lake dune field. These dune fields are not extensive and are separated from the Moses Lake dune field by 20 km. Spectra of the beach and dune sand as well as larger clast samples are similar to those of the fresh surfaces of granodioritic clasts and bedrock indicating similar compositions (Figure 6). There does not appear to be a large basaltic component to the sand based on both visual and spectral analysis. As granodiorite contains only ~ 35 – 50% quartz, this result is not consistent with the $\sim 98\%$ quartz content as determined by Petrone [1970] through visual analysis of Columbia River sand.

4.6. Dunes

[39] Factor analysis was performed on the 39 spectra of dune crest samples (Figure 7) to determine how many independent spectral components are present. Because of the lack of features at short wavelengths and the increased noise level at longer wavelengths, only the 1400 – 450 cm^{-1} portion of the spectrum was used for the analysis. The first

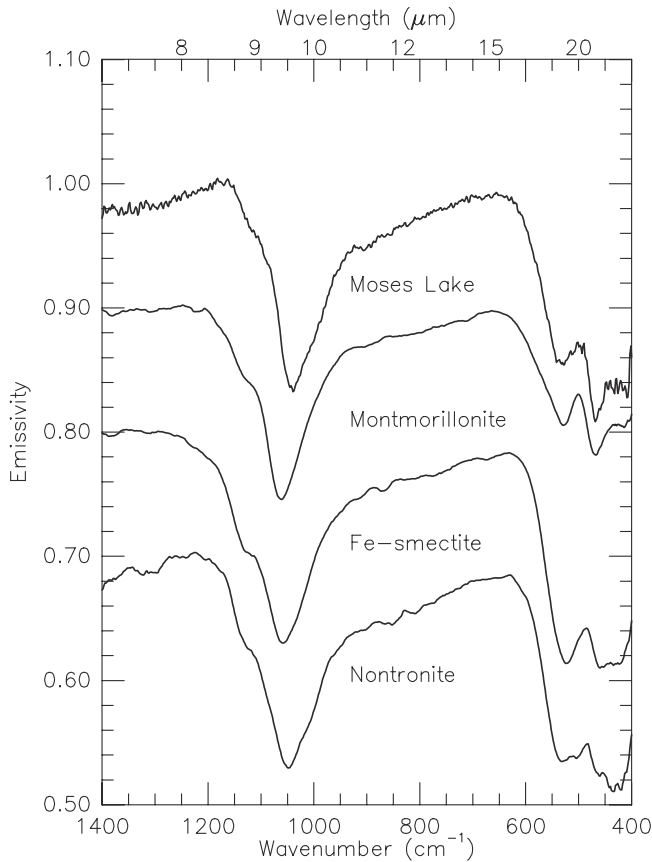


Figure 5. Spectrum of a buried clast surface within the Moses Lake area. This spectral signature compares very closely to several clay mineral spectra and represents a weathering product or coating in this region. Spectra are offset by 0.1 emissivity.

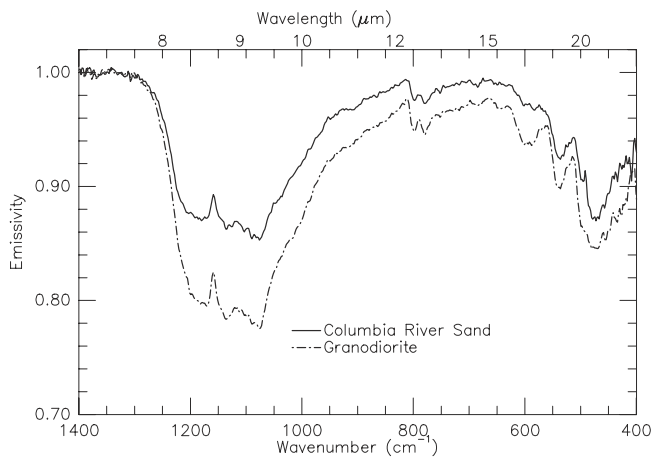


Figure 6. Spectrum of a Columbia River sand sample (solid) taken about 20 km west of the Moses Lake dune field. A sample of granodiorite (dashed) taken from an outcrop near Coulee Dam ~75 km north of Moses Lake is provided for comparison. All spectral features are matched well indicating that the mineralogical compositions are the same. The difference in contrast of the two spectra is due to physical differences between sand and broken rock surfaces.

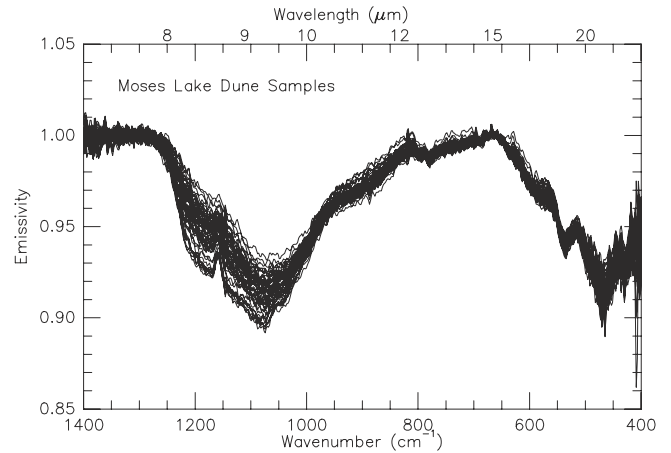


Figure 7. Set of 39 dune crest sample spectra used for the factor analysis and end-member recovery. Note the variation in the strength of the peak near 1150cm^{-1} due to variable amounts of quartz in the samples.

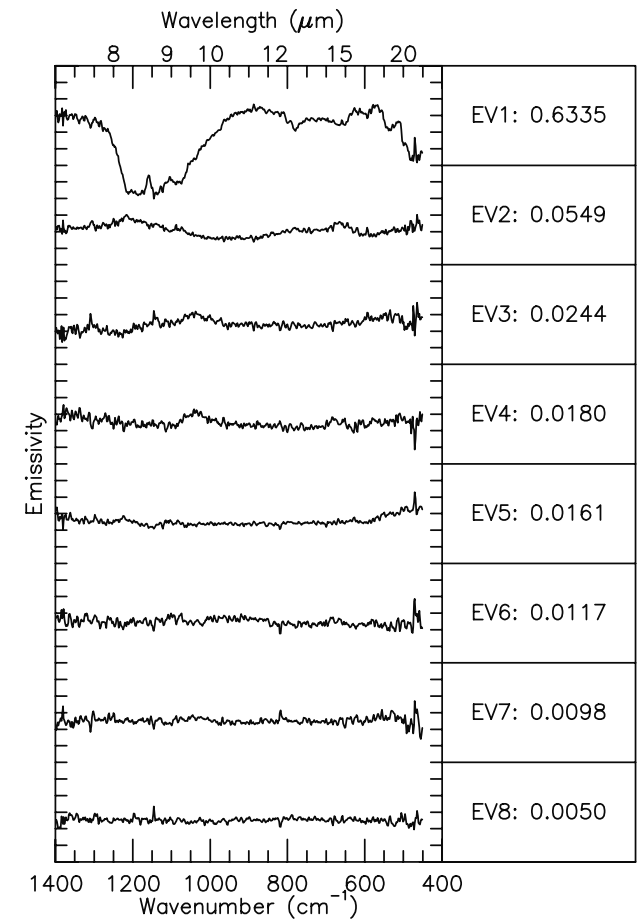


Figure 8. Eigenvectors and eigenvalues 1–8 (listed) derived for the 39 dune crest spectra. Minor spectral information is contained in eigenvectors 2–4. This minor information would be difficult to identify in the variance recorded by the eigenvalues.

eigenvector (eigenvectors are shown in Figure 8) shows significant spectral-like features and the first eigenvalue indicates a significant amount of variance indicating that there are 2 (The mean, which was removed prior to the analysis, represents a component in addition to any significant eigenvectors and eigenvalues.) major components in the system.

[40] There is also some spectral information likely due to mineralogy contained in the next 3 eigenvectors. This spectral information is minor and consistently in the same $\sim 1000\text{--}1100\text{ cm}^{-1}$ region or coincident with the first eigenvector. Since the same general spectral information is repeated in the three eigenvectors, they cannot be used to describe more than one spectral component. While major components that have a large influence upon the spectra are easily separated from the minor systematic noise components introduced into the system, such as noise in the instrument response function used for calibration, minor components are not so cleanly separated [Bandfield *et al.*, 2000b]. As a result, the results of the factor analysis are interpreted to indicate that there are two major spectral components as well as a third minor mineralogical component. Additional minor components are present, but these components represent systematic spectral point to spectral point noiselike components and do not represent realistic compositional components. This minor component may represent a composition present in small concentrations ($<\sim 20\%$) or a spectral component that does not have a large spectral contrast from other end-members present in the system.

[41] The spectral end-members were recovered using 173 pure mineral spectra from the Arizona State University mineral library [Christensen *et al.*, 2000c] as the set of trial spectra and the significant eigenvectors that contain spectral information were fit to these spectra in a least squares manner. In addition, this trial set was augmented by a suite of rock spectra collected by Feely and Christensen [1999] and various rock and mineral spectra collected in the laboratory. This was done to provide as wide a variety of trial shapes as possible in order to increase the chances of end-member recovery if the exact end-member is not present in any of the trial spectra.

[42] The end-member recovery technique was applied using the first 7 eigenvectors and the mean from the set of mixed spectra. Small overestimations of the number of components for the target transformation and end-member recovery does not have a detrimental effect on the results and ensures that all spectral information is included in the system. The dimensionality of the data set is still greatly reduced from ~ 800 (the number of spectral bands used in the analysis) to 8 and eigenvectors that contain only noise will not be preferentially used by the algorithm because combinations of small numbers of eigenvectors that contain only random noise can not adequately reproduce spectral features. The opposite is the case if the true number of spectral components is underestimated. If the system is underestimated by even one component, it may be impossible to accurately recover any spectral end-members. As discussed above, the minor spectral information contained within eigenvectors 2–4 is true spectral information that is contained within the data set and will be used by the algorithm to recover the spectral end-members.

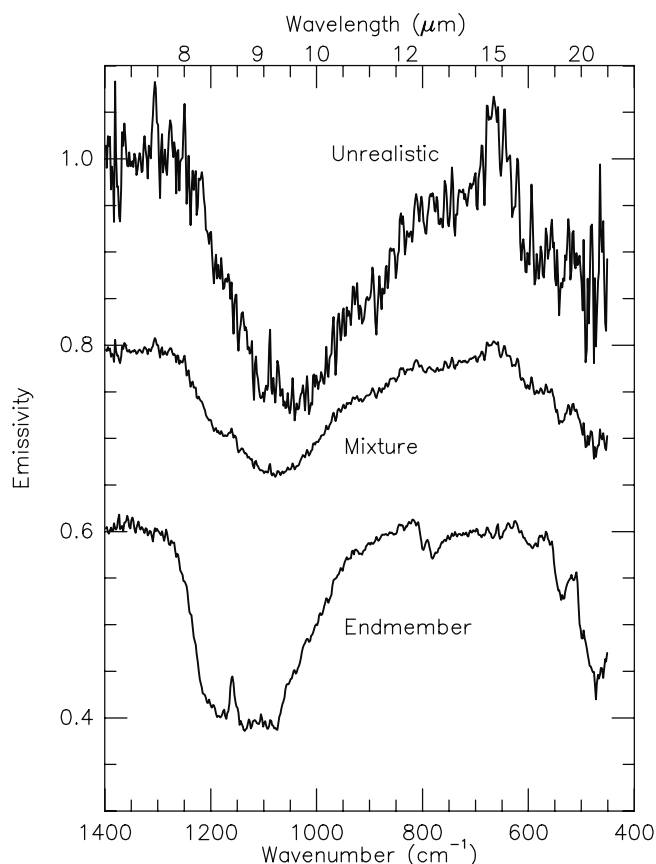


Figure 9. Example of predicted spectra returned from the end-member recovery technique. Unrealistic, mixture, and correct end-member predictions must be manually selected, but may be checked to ensure their accuracy. Spectra are offset by 0.2 emissivity.

[43] Selection of the spectral end-members from the set of best fit shapes was done manually. The several hundred best fit eigenvector combinations returned from the algorithm fell into three basic categories (Figure 9): 1) unrealistic spectral shapes such as those with emissivities >1 ; 2) spectral mixtures that could be modeled as a mixture of positive concentrations of the spectral end-members; 3) spectral end-members. In this manner, three possible spectral end-member shapes were selected (Figure 10).

[44] To obtain end-member abundances in the samples and verify that the correct end-member set was selected, the recovered end-members were used to deconvolve the original dune crest spectra used for the analysis. A summary of this analysis is provided in Table 1. Linear combinations can reconstruct each sample spectrum extremely closely with an average RMS error between the real and modeled spectrum of 0.0018 and a maximum of 0.0027 in emissivity. All derived end-member concentrations are between 0 and 100% and the average concentration sum is 100.08%. In addition none of the three selected spectral end-members could be modeled as a combination of the other two. These results place a high confidence in the accuracy of the recovered spectral end-members.

[45] Two of the recovered spectral end-members from the dune sand sample spectra are very similar in nature to

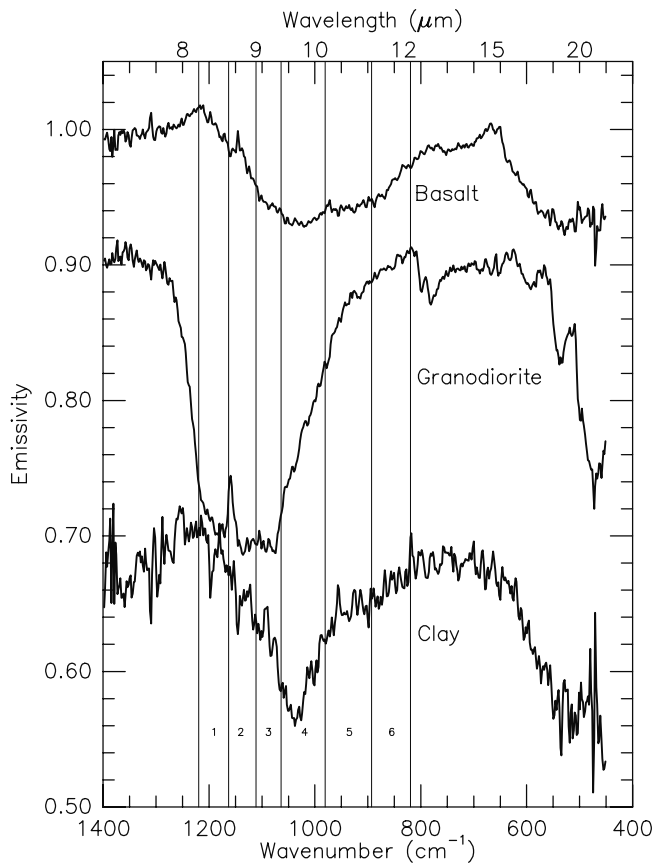


Figure 10. End-members recovered from the dune crest spectral set. Basalt and granodiorite are cleanly separated. The clay end-member is recovered, but is noisy as it is only present at <19% concentrations and only has 15% variability in the spectra. The granodiorite is offset by 0.1 and the clay is offset by 0.3 emissivity. The TIMS band passes are overlaid on the spectra for comparison to the image shown in Figure 11.

the spectra of the basaltic and granodioritic clast and bedrock samples. The spectra of the fresh surfaces of the granodiorite clasts and bedrock match well with one of the recovered end-members, indicating that a component of sand with a granodioritic composition is independently variable (Figure 11a). The other recovered spectral end-member also matches well with the spectra of fresh surfaces of the basalt clasts and bedrock (Figure 11b). The concentrations of the granodioritic end-member vary from 15 to 38% while the range of basaltic composition concentrations varies from 53 to 76%.

[46] The third component contains more noise than the other two and is indicative of a minor component as are the component concentrations which are <19%. This third spectral end-member is very comparable in shape to clay minerals and is similar to the spectrum of a coating on the buried surface of a basaltic clast located within the dune field (Figure 11c). Whether this spectral end-member represents a weathering product that forms on the surface of the sand particles or is present as separate particles is unclear from this analysis.

[47] One of the dune crest samples was divided into 6 grain size fractions between 90 and 710 μm which accounted for $\sim 99\%$ by weight of the sample. The spectra of these size fractions were run through the same analysis as the set of 39 dune crest spectra. Factor analysis indicates that there are 3 components as with the previous analysis. Three end-members were recovered which are nearly identical with the previous analysis as well.

[48] The 3 recovered spectral end-members were used to deconvolve the original grain size spectra. Linear combinations of the three spectral end-members can model the original spectra with low RMS errors, component concentration percentages between 0 and 100% and component concentration sums very nearly equal to 100% (Table 2).

[49] A systematic trend is present in the deconvolution results of the grain size suite spectra as shown in Table 2. There is a clear compositional transition at grain sizes of $\sim 250\mu\text{m}$. The larger grain sizes (250–710 μm) contain $\sim 28\%$ aerial fraction granodiorite and $\sim 62\%$ basalt whereas the smaller grain size fractions (<250 μm) contain $\sim 38\%$ granodiorite and $\sim 53\%$ basalt. The clay spectral end-member is present at concentrations of $\sim 10\%$ in all samples and no significant trends could be established relative to grain size.

Table 1. Deconvolution Results for the Set of 39 Dune Crest Samples

Sample	GD Conc., %	Basalt Conc., %	Clay Conc., %	Sum, %	RMS Error
1	21	67	12	100.15	0.0018
2	28	60	12	100.03	0.0020
3	28	60	12	99.98	0.0020
4	29	55	16	100.03	0.0020
5	23	72	5	99.99	0.0021
6	22	66	12	100.00	0.0019
7	16	71	13	100.04	0.0014
8	20	71	8	99.79	0.0024
9	15	75	10	100.12	0.0020
10	23	66	11	99.93	0.0018
11	19	70	11	99.88	0.0016
12	20	76	4	100.04	0.0020
13	20	69	11	100.04	0.0018
14	23	66	11	100.16	0.0015
15	24	70	6	100.15	0.0019
16	21	66	13	100.19	0.0017
17	24	65	12	100.23	0.0020
18	24	64	12	99.98	0.0020
19	27	65	7	100.10	0.0019
20	19	68	13	100.20	0.0018
21	27	60	13	99.99	0.0022
22	37	60	3	100.18	0.0013
23	17	76	7	100.10	0.0015
24	25	70	6	100.10	0.0015
25	23	67	10	100.08	0.0023
26	31	62	7	100.07	0.0014
27	29	61	10	99.98	0.0019
28	38	59	3	100.09	0.0013
29	30	68	3	100.03	0.0010
30	23	63	14	100.07	0.0017
31	26	61	14	100.42	0.0022
32	24	66	10	100.01	0.0019
33	22	62	16	100.21	0.0017
34	25	62	13	100.18	0.0020
35	34	53	13	99.96	0.0027
36	27	54	19	100.30	0.0013
37	20	63	17	100.17	0.0019
38	23	61	16	99.98	0.0027
39	36	55	9	100.02	0.0017

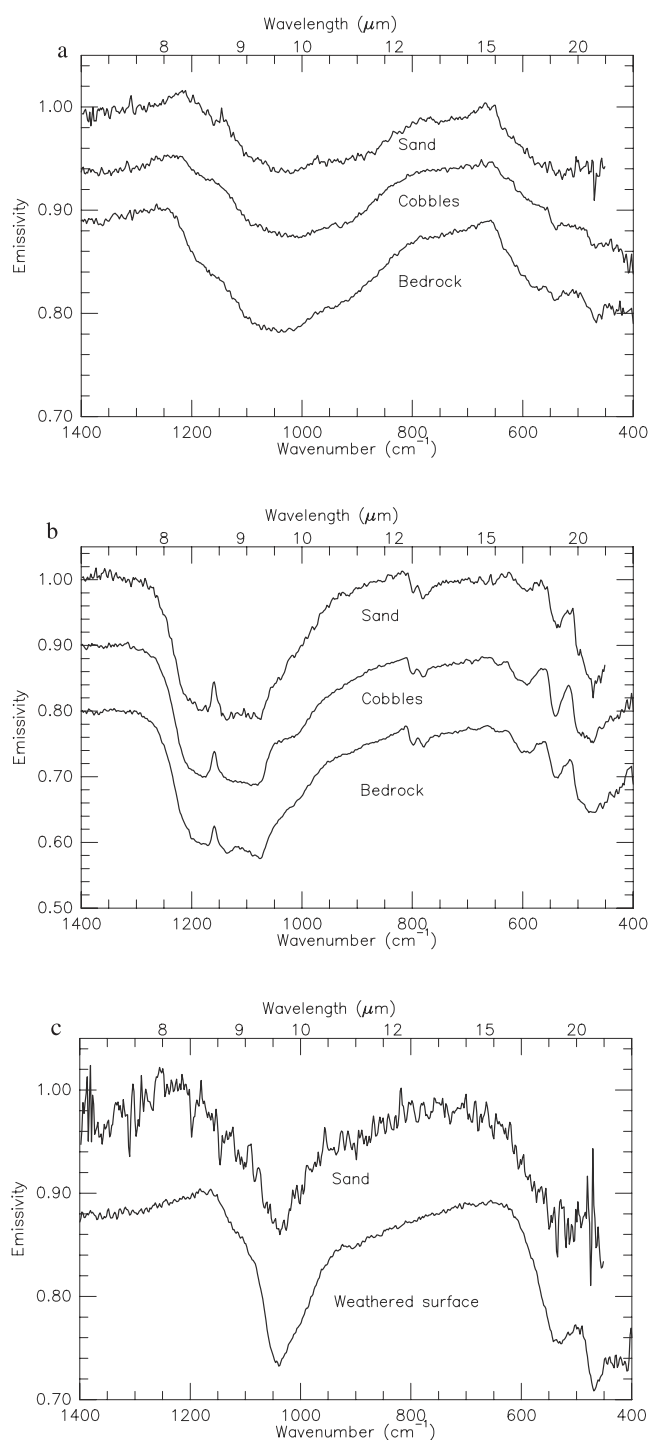


Figure 11. Recovered end-members compared directly with samples in the Ephrata and Grand Coulee areas. All three recovered spectra match local materials and source lithologies. (a) Recovered (sand), clast (cobble), and bedrock spectra of the basaltic composition. (b) Recovered (sand), clast (cobble), and bedrock spectra of the granodioritic composition. (c) Recovered (sand) and weathered surface of the buried cobble (shown in Figure 4).

Table 2. Deconvolution Results for Size Fractions of a Single Dune Crest Sample

Size Fraction, μm	GD Conc., %	Basalt Conc., %	Clay Conc., %	Sum, %	RMS Error	Wt.%
<125	39	52	10	100.52	0.0033	6
125–180	42	53	5	100.35	0.0039	17
180–250	33	54	13	100.45	0.0037	14
250–355	28	63	10	100.27	0.0026	36
355–500	28	63	9	100.59	0.0024	20
500–710	29	60	11	100.28	0.0035	6

4.7. Distributions

[50] The derived component concentrations for each of the 39 dune crest samples were mapped to try to obtain a rough sense of compositional trends. While there appears to be substantial variation in the component concentrations, the spatial distribution of these percentages displayed no obvious regional trend. Attempts failed to locate a larger concentration of the granodiorite end-member toward the west where a possible source of granodioritic sand from the banks of the Columbia River is located. The dune migration is toward the northeast, roughly orthogonal to the Columbia River. To test the possibility of a granodioritic source from the Columbia River, the component concentrations can be plotted as a function of distance from the river (Figure 12). There is no strong compositional trend among any of the dune components, though granodiorite concentrations do increase slightly with increasing distance. This is opposite of what would be expected if the Columbia River is the source of this component.

[51] The processed TIMS image provides more insight into the distribution of the component materials (Figure 13).

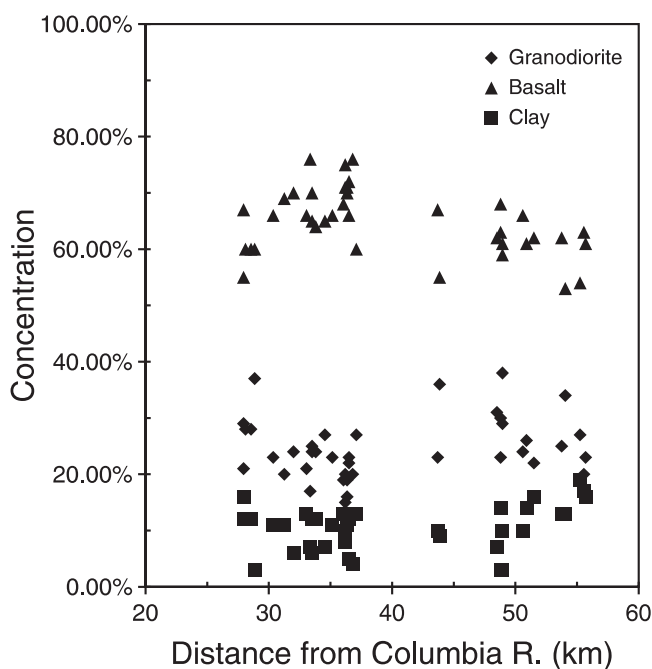


Figure 12. Component concentrations of individual dune samples plotted against the distance from the Columbia River.

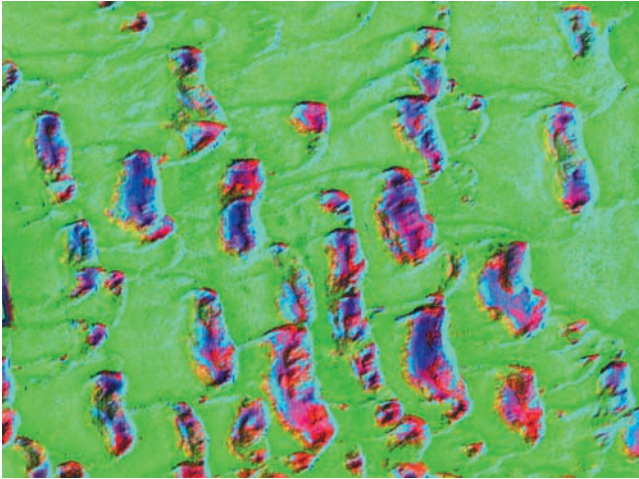


Figure 13. TIMS decorrelation stretch (bands 5-3-1 projected as red, green, and blue) image of a portion of the Moses Lake dune field. Green areas represent volcanic ash from the Mt. St. Helens eruptions. Yellowish areas represent bare soil uncovered by the forward migration of the dune since the 1980 eruptions. Red colors represent relative concentrations of granodiorite and blue represents relative concentrations of basalt. The compositional variation within each dune greatly exceeds that between the dunes. The image is approximately 1 km across.

Figure 9 shows the location of the 6 TIMS band pass filters with respect to the spectral end-members. As there is a significant spectral contrast between each of the spectral end-members present, the TIMS data may be useful in distinguishing variations in the proportion of each of these end-members.

[52] TIMS bands 5, 3, and 1 are projected in the image as red, green, and blue respectively and it is possible to interpret composition based on the color of the image (Figures 9 and 11). As the granodiorite end-member has a large absorption feature coincident with TIMS bands 1 and 3, the granodiorite is projected with relatively low blue and green and a relatively high red level resulting in a red color on the image. The basaltic end-member has a large silicate absorption feature at longer wavelengths coincident with bands 3 and 5 and is consequently a blue color on the TIMS image.

[53] Interdune areas consist primarily of vegetation and ash deposits from the Mt. St. Helens eruption. Both of these materials are relatively featureless in the TIMS wavelength range compared to the dune spectral end-members and, as a result of the decorrelation stretch, are projected as green on the image. The soil, which does not contain the same spectral signature as the recovered clay end-member, contains an absorption that is coincident with band 1 and is yellow-orange on the TIMS image.

[54] Immediately noticeable in the TIMS image is a considerable compositional variation within each dune. The slipface and farthest portion of the stoss are blue, indicating a relatively basaltic composition. The crest and stoss immediately behind the crest varies from red to purple, indicating a variable, but relatively granodioritic composition. Immediately behind each of the dunes is an orange

colored strip that represents the soil uncovered by the forward migration of the dune since the ash was deposited from the Mt. St. Helens eruption in 1980.

[55] As with the laboratory compositional percentages, the TIMS data do not show any sign of a regional pattern of compositional distribution within the dune field. There is no noticeable increase in a granodioritic composition toward the possible source of the Columbia River sands to the west nor are there any interdune local concentrations of any of the end-members. The majority of compositional variation is located within each dune.

5. Discussion

[56] The application of the factor analysis and end-member recovery techniques has identified three components in the dune sand: basalt, granodiorite, and a minor clay component. Each of these components may be identified through comparison to common terrestrial rock and mineral spectra. The eigenvector and eigenvalue analyses as well as the ability to closely model spectra of all 39 dune samples using linear combinations of these three end-members indicates that these components are combining in a linear manner. Minerals within each component are varying in unison and are probably of similar grain size. While this may be expected for the basaltic component that is composed primarily of groundmass where crystal size is much smaller than grain size, it also holds true for the granodioritic component where crystal size is typically much larger than the grain size of the sand. This means that while the sand grains are individual minerals such as feldspar and quartz, they are likely of similar grain size and distributed by the wind in the same manner. As a result, their apparent composition is not skewed from the original source bedrock.

[57] The spectral similarity between the isolated sand components and fresh surfaces of the larger clast size deposits and bedrock outcrops within the Grand Coulee indicates that these components are compositionally similar and may be linked. The abrasive nature of the dune environment continually scours grain surfaces providing relatively fresh, unaltered surfaces that are not available on the larger clast deposits. Even bedrock exposures, such as samples from steep cliff walls, tend to have more weathering on their surfaces than the dune sands. Light amounts of alteration products (<20 areal%), in the form of clays such as montmorillonite or iron smectite, are present and identifiable in the dune samples, however these products and their effects may be isolated from the other components. It is not clear if these alteration products are present as individual grains or as rinds or coatings on either the basalt or granodiorite grains. Because eolian environments actively keep themselves relatively free of dust, weathering products and vegetation, they provide an ideal surface for thermal infrared remote determination of composition.

[58] The TIMS image (Figure 13) demonstrates the ability to distinguish between these dune components using a multispectral thermal imager using standard image processing techniques. The image format of this data set provides information on the distributions of the compositions that would otherwise be difficult to determine using either field

observations or samples collected and analyzed in the laboratory. Although it is impossible to obtain precise compositions using the 6 band TIMS pixels, felsic versus mafic versus soil compositions may be distinguished and correlated with the isolated end-member component.

[59] The lack of any regional concentrations of the granodiorite and basalt components within the dune field indicates that both compositions were most likely deposited simultaneously during flood events. It is not clear what the cause of the variation in composition of each of the 39 samples is, though a likely cause is local variations in particle size within each dune. As seen in Figure 13, though the general trend of intradune compositional variation is clear, there are also clearly minor deviations from this trend. There is no indication of a separate source of granodiorite. While the Columbia River is a potential source for the granodiorite sand and there are numerous local dunes in the region, its physical separation of ~ 20 km as well as the relative isolation of Columbia River dune sands make it an unlikely source. In addition there is no indication of increasing concentrations of granodiorite in the Moses Lake dune sands toward the Columbia River to the west (Figure 12). The granodioritic bedrock upstream from both the Columbia River and the Grand Coulee where they meet at the Coulee Dam is a source for both deposits.

[60] The spectral similarity does not necessarily prove common progeny, especially with common compositions such as basalt and granodiorite. However, the commonality of the mineralogies and the lack of a clear compositional trend combined with the source possibilities of the Columbia River or the Grand Coulee, more clearly points to the Grand Coulee as the source. There are clearly granodioritic source materials within the coulee, granodioritic clast deposits mixed with basaltic deposits, and no clear regional trend of sand composition nor any clear evidence that sand is being transported from the Columbia River. There is also no reason the granodiorite concentration should increase in the upstream direction, since all of the sand, basaltic and granodioritic, from the outflow floods will have been deposited simultaneously regardless of where it was picked up within the Grand Coulee.

[61] Subsequent development of the dune field has separated the basalt and granodiorite components within each dune. The basalt has higher concentrations at grain sizes larger than $250\mu\text{m}$ and the granodiorite shows higher concentrations at grain sizes less than $250\mu\text{m}$. This allows the wind, which preferentially concentrates smaller particle sizes at the crest of the dune, to separate the two initially well-mixed compositions within each dune. As a result, the basaltic component has higher concentrations on the slip-face and rearward portion of the stoss while the granodiorite displays higher concentrations on and near the crest of the dune. The longer transport distance to the granodioritic source may account for its generally smaller particle size distribution.

[62] This wind driven separation of compositions can be seen in TIMS images of several other dune fields. Though there are clearly distinguishable sources of materials in the Kelso dune field in the Mojave Desert in California [Ramsey *et al.*, 1999], the images also display significant compositional variation within the individual dunes. This phenomenon is also clearly visible in data sets from the

Great Sand Dunes in Colorado as well as Christmas Valley in Oregon [Edgett and Christensen, 1995]. This variation may help isolate and identify source lithologies and transport histories in regions where there is no regional pattern of compositional distribution or there is limited coverage of remote-sensing data or sample collection.

[63] In isolated regions or on other planets where it may be impossible to sample or even view potential bedrock sources, the similarity of the spectra of sand and source materials allows for the identification of the composition of the local or regional bedrock [e.g., Bandfield *et al.*, 2000a; Christensen *et al.*, 2000a, 2000b, 2000c]. This is essential for determining the volcanic history of the Martian surface where basaltic and andesitic sands may be linked to bedrock that is often either covered or mantled.

[64] Future higher spatial resolution instruments may be able to identify other compositions within each dune. THEMIS, which contains a 9 band, 100 m/pixel thermal infrared imager to fly on the 2001 Mars Odyssey orbiter will provide both the spatial and spectral resolution needed to determine if this compositional segregation occurs on Martian dunes. The miniTES instrument, a 8 or 20 mrad field of view 10 cm^{-1} spectral sampling spectrometer, will be carried on the 2003 Mars Exploration Rovers and have the potential to raster hyperspectral image cubes of the local scene. This sort of coverage will provide the ability to isolate and identify detailed compositions of multiple sand components, including source lithologies and any weathering products present. The TES instrument has already shown variability in composition of intracrater sands at the limit of its spatial resolution ($\sim 3 \times 8$ km) [Wyatt *et al.*, 2001].

[65] A wealth of Earth based thermal infrared data sets from both airborne and space platforms, such as TIMS, ASTER, and MASTER, are currently available for Earth remote sensing. These data sets along with the methodology presented here may be used to study and understand dune processes worldwide.

6. Conclusions

[66] The application of thermal infrared remote sensing and laboratory spectroscopy as well as in situ field observations has demonstrated the following:

- Factor analysis and end-member recovery techniques can be applied to dune samples in order to isolate mineralogical sand components.
- The compositions of the isolated sand spectral components may be identified and linked to larger clast deposits as well as source bedrock lithologies.
- Weathering and coating components may also be isolated and identified in the dune sands although their concentrations are low (<20 areal%) due to abrasion in a vigorous eolian environment.
- While hyperspectral measurements are needed to obtain precise mineralogical compositions, multispectral thermal infrared imagers may clearly distinguish components and provide a rough estimate of composition.
- The Moses Lake sand dunes consist of significant amounts of both granodiorite and basalt compositions that were probably deposited simultaneously with no local concentrations of either composition. Both the basalt and

granodiorite lithologies present in the Grand Coulee are compositionally similar to the larger clast sizes present on the Ephrata Fan as well as the components present in the sand.

- Subsequent development of the dune field has separated the basalt and granodiorite components within each dune. Dune crests contain higher concentrations of granodiorite than slipfaces and farthest portions of the stoss because smaller grain sizes (<250 μm) contain higher concentrations of the granodiorite.

- While the Columbia River is a potential source for the granodioritic sand of the Moses Lake dunes, its physical separation (~20 km to the west) and the lack of increasing granodiorite concentrations toward the river make this possible source unlikely.

[67] These techniques are ideally suited for multi and hyperspectral thermal infrared spectrometers and imagers such as ASTER, MASTER, TIMS, TES, THEMIS, and miniTES for determining transport histories, weathering environments, and source lithologies.

[68] **Acknowledgments.** The authors wish to thank Wendy Calvin for a helpful review that significantly improved and clarified this manuscript. Michael Kraft participated in discussions helping to keep the spectroscopy tied to reality. Teresa Longazo produced the size fraction samples used in this work.

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