Modelling the Transmission Component in TIR Reflectance Spectra of Sandstones to Understand the Effect of Surface Roughness and Clinging Fines

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Abstract Surface roughness of rocks influences the spectral shape and amplitude of thermal infrared spectra, but the relationship is poorly understood. This research aims to understand the physical processes that cause the observed spectral variation by modeling the reflectance spectra with a nonlinear transmission model. We designed a model that combines rock surface reflection with transmission through clinging fines that coat the surface. The novelty of this approach is that it does not model individual particles, but compiles different combinations of thin particle transmission and reflectance of the solid surface until it has an optimal fit with actual measured rock spectra. We use directional-hemispherical reflectance spectra of two quartz sandstones with a varying surface roughness, a transmission spectrum of a powder from one of these sandstones, and a pure mineral (kaolinite) transmission spectrum as input for the model. The model reproduces spectral amplitude and shape of the principal quartz reststrahlen doublet of three out of four measured sandstone spectra. It also correctly displays the strong bands of the quartz reststrahlen doublet. With the model we demonstrate that reflectance and transmission based modeling is a promising technique for identification and correction of spectral characteristics that result from a different surface roughness.

Plain Language Summary The roughness of geological rock samples influences the results of thermal infrared spectral measurements, changing both the amplitude and the shape of a spectrum. A possible explanation for this effect is the occurrence of transmission through very fine particles. However, the relationship between the roughness and the degree of change in the spectra is not yet clearly defined. We designed a model that combines the reflectance of rock surfaces with transmission through very fine, small particles called “clinging fines” that partly coat the surface. This approach is innovative because the model combines transmission through fine particles with reflection of the underlying rock surface. As model input we use reflectance spectra of two quartz-rich sandstones with surfaces that vary in roughness, a transmission spectrum of a powder of one of these sandstones, and a transmission spectrum of a pure clay mineral (kaolinite). The goal of the model is to create a spectrum to has an optimal fit with the spectrum of rock surfaces that suspectedly have been influenced by transmission. We demonstrate that a model based on reflectance and transmission is a promising technique for the identification and correction of spectral differences that result from variations in surface roughness of rocks.

1. Introduction

In the context of laboratory-based geological spectroscopy, several researchers showed that surface roughness of rocks influences thermal infrared (TIR) spectral signatures, both in spectral shape and in amplitude (Hardgrove et al., 2016; Kirkland et al., 2002, 2003; Osterloo et al., 2012; Rost et al., 2018; Salisbury & Wald, 1992). The shape and amplitude (Figure 1) in thermal infrared (TIR) spectra play a critical role in determining the mineral composition of rock samples and drill cores. Particularly when using modern (imaging) spectrometers of high spectral resolution subtle spectral differences become increasingly more relevant as these affect mineral quantification. The relationship between surface roughness and resulting spectral shape and amplitude is poorly understood; there is no agreement in literature on a physical explanation. Some mentioned surface cavities as the main driver (Ramsey & Fink, 1999), while others claimed that it is caused by surface (micro)topography variation (Hardgrove et al., 2016; Osterloo et al., 2012) or a combination of both (Kirkland et al., 2002). Others
explained this relationship with so called “volume scattering” where transmission of light through thin edges of a rough surface or through ultrafine particles known as “clinging fines” (ultrafine particles <10 μm attached to the surface of coarser grains; Rost et al., 2018; Salisbury & Wald, 1992).

Historically, much work has been done to explain the effect of grain size and packing density of particles on the spectral behavior of mineral powders (Arnold, 2014; Aronson & Emslie, 1973; Conel, 1969; Glotch et al., 2016; Hapke, 1993, 1996; Hardgrove et al., 2016; Ito et al., 2017; Mackowski & Mishchenko, 2011; Moersch & Christensen, 1995; Mustard & Glotch, 2019; Mustard & Hays, 1997; Pitman et al., 2005; Shkuratov et al., 1999; Wald & Salisbury, 1995). Most of these models were computed in the context of planetary research, and are, therefore, emission based.

Conel (1969) was among the first to model the emissivity of regoliths, by linking Mie theory to the scattering properties of quartz powders and input these into a radiative transfer (RT) scattering model. This so-called “cloudy atmosphere model” from Conel (1969) showed that Mie theory can be used to model surfaces with relatively closely packed particles with some success. The model predicts the depth of new bands and local spectral curvature and shows that particles smaller than ½ μm in diameter act as black emitters. Furthermore, the model shows that powdering reduces spectral contrast and new spectral features appear when particle sizes are reduced to order of microns.

Moersch and Christensen (1995) showed that so-called Hapke theory-based models (Hapke, 1993), that assume irregular grain shapes, work best for particles with a radius larger than the wavelength while spherical grain Mie theory models work best for particles that are smaller than the wavelength. They compiled a Mie/Hapke hybrid model that calculates the single-scattering albedo with Conel’s cloudy atmosphere model and apply a diffraction subtraction correction (Wald, 1994; Wald & Salisbury, 1995) to account for close packing. This model correctly predicts spectral behavior in strong bands, works well for weak bands (Figure 1) and models intra-band regions reasonably well by approaching absolute emissivity. It also correctly predicts the emissivity maximum of the Christiansen frequency (Figure 1). However, modeling the reststrahlen feature (8–10 μm) of quartz proved to be too complex for the model because it underestimates the magnitude of spectral change for strong bands, which they attribute to errors in the published values of the used optical constants of quartz (Spitzer & Kleinman, 1961).

Moersch and Christensen (1995) showed that the Mie/Hapke hybrid model best approximates measured spectra. Their model predicted spectral behavior in strong bands that have high reflectance values, as well as weak bands that have low reflectance values. It also predicted the emissivity maximum of the Christiansen frequency.

Mustard and Hays (1997) tested the hybrid Mie/Hapke scattering model proposed by Moersch and Christensen (1995). They applied it to fine particle reflectance spectra of olivine and quartz, by calculating the single-scattering albedo with Mie theory and then used the Hapke (1981) bidirectional reflectance model to calculate reflectance. For olivine their model worked reasonably well: They were able to reproduce changes to the Christiansen frequency, reststrahlen bands, and transparency features that were observed in the olivine laboratory spectra. However, their modeled spectra for quartz were similar to those of Moersch and Christensen (1995), and did not accurately reproduce the band strengths and changes in reststrahlen bands seen with changes in particle size. They showed with quartz as particle size approached the wavelength of light, very different behavior was observed. Mustard and Hays (1997) most likely explanation for this discrepancy is that large n and k values (optical constants) are problematic either for Mie theory or Hapke’s reflectance model. Also, they only observed this with quartz because their absolute values for optical constants of quartz were about two times those of olivine. While both Moersch and Christensen (1995) and Mustard and Hays (1997) did not achieve the correct spectral amplitudes with their Mie/Hapke model, spectral trends linked to particle size variation in quartz and olivine were well modeled and showed the need for a hybrid Mie/Hapke model.

Wald and Salisbury (1995) improved the Mie theory model by adding a Heney-Greenstein approximation, including both sets of optical constants of quartz, and using the diffraction subtraction approximation to account for close packing in large particulate samples. They successfully model thermal infrared emissivity spectra of coarse grained quartz sand but failed to model fine-grained sand. They attributed this to inappropriate model assumptions, such as the neglect of clinging fines, close-packing effects and an unknown effect of particle shape. Wald and Salisbury (1995) have also questioned the validity of the quartz optical constants and indicate that there is some error in the values, which likely greatly impacts modeling of fine particles. Pitman et al. (2005) presented a hybrid Mie theory/numerical RT model for emissivity spectra of micrometer-sized quartz powders. They use
Mie theory to calculate the single-scattering properties of quartz grains which were input into a numerically exact discrete ordinates multiple scattering RT model (Mustard & Glotch, 2019; Stamnes et al., 1988). This model however lacked a realistic treatment of particle shape variation and closely packed grains, resulting in an overcorrection of the modeled spectra with the diffraction subtraction correction (Wald, 1994; Wald & Salisbury, 1995) and the static structure factor correction (Mishchenko, 1994). Instead, they suggest to discard Mie theory in favor of more complex grain shapes (i.e., a model that does not expect perfectly spherical grains as in Mie theory).

To model multisphere systems, the multiple sphere T-matrix model (MSTM; Mackowski, 1994; Mackowski & Mishchenko, 1996, 2011) was developed as an extension of Mie theory. Unlike Mie theory, it models close packing of spheres by calculating scattering properties which are input into RT models. It requires optical constraints of mineral positions of spheres in a cluster, and size parameters at every wavelength of interest as input. This model is able to control the size, position, composition (via assigned optical constants), and packing density of clusters of particles. However, as in Mie theory, particles are presented as perfect spheres, which may represent a major source of error (Mustard & Glotch, 2019; Pitman et al., 2005).

More recent work combines light scattering and RT models that substantially improve upon the Mie/Hapke approach (Glotch et al., 2016; Hardgrove et al., 2016; Ito et al., 2017). Both Glotch et al. (2016) and Hardgrove et al. (2016) use a hybrid multiple sphere T-matrix model (MSTM)-Hapke model to model thermal infrared (TIR) scattering of halite-silicate mixtures, and solid microcrystalline quartz, respectively. The models are set up analogously to the Mie/Hapke hybrid model (Moersch & Christensen, 1995; Mustard & Hays, 1997), but the scattering properties were derived from the multiple sphere T-matrix model (MSTM) model (Mackowski & Mishchenko, 2011) and emissivity was calculated from the Hapke (1996) thermal emission model. The model from Glotch et al. (2016) accurately reproduced the shift in Christiansen frequency position observed with increasing salt content in the halite-silicate mixtures, as well as the overall changes in spectral shape (Mustard & Glotch, 2019). The model from Hardgrove et al. (2016) can reproduce the observed effects of surface roughness on the order of the wavelength of light. They successfully modeled the effect of crystal size and surface

Figure 1. Quartz spectrum (polished spectrum of the pure quartz sandstone): strong bands marked blue, weak bands marked orange and the Christiansen frequency (a) at 7.4 μm and the reststrahlen doublet (b) at 8–10 μm. The right lobe of the reststrahlen doublet has the most profound spectral contrast (arrow) with an amplitude of reflectance of 0.70 in this particular case.
roughness on thermal emission spectra of solid micro- and macrocrystalline sediments with a distinct surface roughness variation, including the spectral shape and contrast in the reststrahlen band region.

Arnold (2014) and Ito et al. (2017) conducted comparisons of the Mie/Conel, Mie/Hapke, MSTM/Conel, and MSTM/Hapke hybrid models. Arnold (2014) showed that for fine grain sizes of silica glass (2 and 19 μm), the MSTM/Hapke model provides a better fit to measured emissivity spectra compared to the Mie/Hapke model. For coarser particulates (179 μm and to a lesser extent the 49 μm size fractions), multiple scattering is substantially reduced, therefore both the Mie/Hapke and MSTM/Hapke models provide relatively good fits to the measured emissivity spectrum. This was confirmed by Ito et al. (2017) who stated that the MSTM/Conel and MSTM/Hapke hybrid models best modeled emissivity spectra of the finest particle size of enstatite in the 400 to 1,300 cm⁻¹ range (7–25 μm). Also, they concluded that the T-matrix hybrid models were generally more consistent with laboratory measurements than the Mie hybrid models and demonstrate that a more realistic treatment of light scattering in closely packed media with particle size comparable to the wavelength of light can improve modeling quality.

The models described above (Arnold, 2014; Conel, 1969; Glotch et al., 2016; Hardgrove et al., 2016; Ito et al., 2017; Mackowski & Mishchenko, 2011; Moersch & Christensen, 1995; Mustard & Hays, 1997; Pitman et al., 2005; Wald & Salisbury, 1995) all managed to successfully model some aspects of emissivity or reflectance spectra. Either it be the modeling of coarser particulates or modeling the spectra of a specific mineral. However, modeling the finest particle sizes often proved challenging, especially the reststrahlen feature that encompasses the most prominent spectral features. A possible major source of error for fine particle modeling is the computed optical constants (n and k), which is suggested by multiple groups (Moersch & Christensen, 1995; Mustard & Hays, 1997; Wald & Salisbury, 1995). The optical constants of a mineral are wavelength dependent and a uniform well-documented library of optical constants in unavailable (Mustard & Glotch, 2019). Laboratory investigators showed that optical constants can be derived by inverting Hapke and Shkuratov models (Li & Milliken, 2015; Sklute et al., 2015). However, these inversions require that the particle size, and in the case of the Shkuratov model, the porosity of the material is well known (Mustard & Glotch, 2019). Lastly almost all previous models are based on emissivity spectra of mineral powders. Except for Hardgrove et al. (2016) and Mustard and Hays (1997), which focus on reflectance of quartz and olivine powders and emissivity of solid microcrystalline quartz, respectively. It is unclear whether these models could be readily applied to model the effect of surface roughness of solid rock samples in the TIR reflectance domain. Furthermore, Rost et al. (2018) have shown that the spectral changes due to surface roughness differences can manifest themselves in the reststrahlen feature. None of the above models could convincingly model this feature.

In Rost et al. (2018), our laboratory measurements showed that different rock sample preparation methods (i.e., split, saw or polish) resulted in differences in surface roughness which significantly affected the shape and amplitude of reflectance spectra. Figure 2 shows the spectra of the pure quartz sandstone and the quartz/clay sandstone from Rost et al. (2018). This figure illustrates that surface roughness differences resulted in significant variations in spectral amplitude for the quartz reststrahlen doublet. The shape of the reststrahlen feature varied with a changing surface texture as well. Three of the six spectra contained a so-called “horn feature”: The left lobe of the reststrahlen doublet had its reflectance maximum at a longer wavelength associated with quartz absorption (Figure 2a I and II; Salisbury & D’Aria, 1992). Additionally, a small spectral feature or sharp nick was observed at ~9 μm in the spectrum of the split surface Figure 2b III). This small spectral feature has also been observed in other quartz-rich rocks with small percentages of kaolinite (Salisbury et al., 1994).

We aim to understand the physical processes that cause the observed variation in spectral shape and amplitude by modeling the reflectance spectra with a newly designed non-linear transmission model. The model combines rock surface reflection with transmission through clinging fines that coat the surface. The novelty of this approach is that we avoid modeling individual particles, but compile different combinations (our so-called “components”) of thin particle transmission and reflectance of the solid surface until we have an optimal fit with actual measured rock spectra. With this approach we do not need complex light scattering or RT models and, thus, we can avoid error that originates from the wavelength-dependent optical constants. We focus solely on the effect of clinging fines and do not incorporate the effect of surface cavities or (micro)topography to test if only clinging fine-based modeling can explain the spectral changes observed in measurements described by Rost et al. (2018).
We use directional-hemispherical reflectance spectra of the two quartz sandstones with a varying surface roughness from Rost et al. (2018), a transmission spectrum of powders from one of these sandstones, and a pure mineral (kaolinite) transmission spectrum as input for our model. We compare our model results to actual measurements and validate our findings by characterizing the surface of our samples with scanning electron microscopy (SEM) imaging to determine grain size distribution and surface texture and to confirm the presence of clinging fines at the surface of the rocks.

2. Theoretical Framework

2.1. Optical Processes

When light rays interact with a geological surface or particles they will be (partly) reflected, transmitted or absorbed depending on the wavelength of the light, the angle of incidence and the optical constants of the encountered material. In addition, the particle radius, surface roughness and number of surface cavities also influence the interaction with the incoming light (Mustard & Hays, 1997).

The optical constants of a material consists of the real refractive index \( n \) and imaginary refractive index \( k \), which both depend on the wavelength of the incoming light. The real refractive index is a measure of the speed and propagation direction (i.e., bending) of a light ray when passing from one medium to another and is determined by Snell's Law. The imaginary refractive index, also known as the absorption or extinction coefficient, is a measure of how strongly the material absorbs light at a specific wavelength. Both optical properties can be calculated by measuring the transmission of light through a material with a known thickness. The real refractive index \( n \) can be deducted from the change of the speed of light when it passes through the material and the imaginary refractive index \( k \) can be measured with Lambert-Beer law by calculating the ratio of the incoming and outcoming light which is proportional to the absorption in the material (Hummel, 2011). For TIR wavelengths, where \( k \) is large, the number of principal complex refractive indices of a mineral needed to fully model its spectral anisotropy varies with the crystal symmetry (Mustard & Glotch, 2019).
In the strongly absorbing reststrahlen regions, where \( k \) is large and the light cannot propagate through a sample, a decreasing particle size reduces the spectral contrast due to multiple surface scattering (Mustard & Glotch, 2019). As the particle size further decreases and the particle radius becomes smaller than the wavelength (\( D \ll \lambda \), Rayleigh scattering; Hapke, 1993), the light can penetrate further into the particle, resulting in an increasing absorption and an overall lowering of the reflectance (Mustard & Hays, 1997). Due to the source of the returned light, the phenomenon is known as volume scattering. With such fine particles, the competing effects of surface scattering versus volume scattering results in a nonuniform change in reflectance, affecting the spectral shape of the reststrahlen features (Mustard & Glotch, 2019).

Additionally, at short wave infrared (SWIR) and near infrared (NIR) wavelengths \( k \) values are orders of magnitude lower than at TIR wavelengths. Therefore, as particles become finer they will first move out of the geometric optics regime and into the Mie or Rayleigh scattering regime at TIR wavelengths before they do at short wave infrared (SWIR) and near infrared (NIR) wavelengths. The result is that ultrafine grains (<10 μm) become optically thin for the TIR wavelength range, and volume scattering dominates over surface scattering (Vincent & Hunt, 1968). Furthermore, transparent grains allow photons to interact with underlying mineral surfaces, which can result in non-linear spectral mixing behavior if volume scattering dominates (Ramsey & Christensen, 1998; Salisbury & Wald, 1992; Thorpe et al., 2015).

2.2. Surface Roughness and the Cavity Effect

An increase in surface roughness affects TIR spectra, causing a reduced spectral contrast and a changing spectral shape (Hardgrove et al., 2016; Kirkland et al., 2003; Osterloo et al., 2012; Rost et al., 2018). Kirkland et al. (2003), showed that microscopic surface roughness introduces volume scattering and the cavity effect, which they link to a reduced spectral contrast. Surface cavities can act as light traps by trapping and absorbing incident light rays and reducing reflection and the accompanying spectral contrast. This phenomenon is known as the “cavity effect” and is influenced by the cavity shape, area, entrance aperture area, and the reflectivity of the cavity wall (Bedford et al., 1985; Kirkland et al., 2003; Osterloo et al., 2012). The relationship between the decrease of the spectral contrast and the increase of the number of cavities is approximately linear. For most materials, the increase in surface roughness results in an increase in the number of surface cavities.

Osterloo et al. (2012) show that as roughness increases, the resulting spectral contrast decreases. The authors attribute this to a partial loss of energy as a result of volume scattering. They also suggest that further increasing roughness does not result in a continued decrease in spectral contrast, as a result of multiple reflections of light within surface grains that increase total reflection. Hardgrove et al. (2016), show that surfaces that are rough on a wavelength scale result in distinct spectral contrast variation and suggest a relationship between the crystal size and the surface roughness.

3. Data and Methods

In this section we give a short description of the characteristics of the two sandstones used for this research, followed by a description of the spectral reflectance measurements and results from Rost et al. (2018, Figure 2) and the transmission measurements and the scanning electron microscopy images obtained for this research. At the end of this section, we present our model.

3.1. Characteristics of Sandstones

We selected two quartz sandstones because most modeling of mineral powder spectra has been conducted on quartz powders (Moersch & Christensen, 1995; Mustard & Hays, 1997; Pitman et al., 2005; Wald & Salisbury, 1995). The selected samples are a pure quartz sandstone with a porosity of 6%, determined by the supplier with a DarcyLog (Fontainebleau sandstone from cydarex.fr; Bourbie & Zinszner, 1985; Egermann et al., 2005), and a quartz/clay sandstone with 1% clay (kaolinite, determined with quantitative x-ray diffraction; Rost et al., 2018) with a reported porosity of 20% (Gildehaus sandstone; Reyer & Philipp, 2014). Rost et al. (2018) achieved a variation in surface roughness for the spectral reflectance measurements, by splitting, sawing or polishing three different surfaces of each sample. The samples were sawed to the appropriate size with a Lortone LSS-14P lapidary diamond saw. Sample surfaces were polished with a Knuth Rotor polishing machine that uses
silicon carbide grinding papers. Stepwise polishing was done by increasing the grinding paper smoothness from an 80, 220, or 500 grit to a 4,000 grit. The sample was split with a brick cutter. The sample planes have parallel orientation in the original sample block with a maximum spacing of 20 cm, to avoid influences from differences in (mineral) orientation, sample heterogeneity and small lateral changes in sample composition (e.g., porosity). The samples were oven-dried at 50°C for at least 8 hr. We placed the samples in a desiccator during cooling, to prevent atmospheric H₂O from entering the samples. Details of the instrument, measurement setup and spectral processing are given in Rost et al. (2018) and Hecker et al. (2011).

3.2. Spectral Measurements

We use the directional-hemispherical reflectance (DHR) spectra from Rost et al. (2018) measured on a Bruker Vertex 70 Fourier transform infrared (FTIR) spectrometer. This is a non-imaging spectrometer with a custom-made diffuse gold-coated integrating sphere and mercury-cadmium-tellurium detector, which is purged with N₂ gas (100 L/hr) to avoid atmospheric H₂O from interfering with the measurements. We used a spectral range of 1,660–690 cm⁻¹ (6–14.5 μm) at a resolution of 4 cm⁻¹ since this range covers the diagnostic reststrahlen features related to fundamental vibrations in silicate minerals (Salisbury & Vergo, 1991). Apart from varying sample surface treatment that led to different surface roughness, all parameters were kept constant. The presented spectra are an average of nine measurements acquired on different spots of the sample surface.

In addition to reflectance spectra, we also obtained transmission spectra with a platinum diamond micro-attenuated total reflectance (ATR) accessory mounted on a Bruker Vertex 70 Fourier transform infrared (FTIR) spectrometer. This is a single reflection diamond attenuated total reflectance (ATR). To prepare the sample material, we powdered rock samples with a Retsch ball mill and dry-sieved resulting in a grain size fraction of <180 μm. Further sieving of smaller fractions was not performed to avoid separating minerals that have a larger grain size and thus would potentially change the composition of the powder. We used the spectral range of 1,660–690 cm⁻¹ (6–14.5 μm). The presented spectra are the average of five spectral measurements.

The transmission spectra of the two powdered sandstones have different spectral shapes (Figure 3, the green and blue spectra). The transmission spectrum of the pure quartz sandstone shows characteristic absorption and reflection features at wavelengths that match those of a pure quartz transmission spectrum from the Johns Hopkins University spectral library (Figure 3, green and brown spectra, respectively), suggesting they have a comparable composition. The transmission spectrum of the quartz/clay sandstone sample shows spectral features of quartz as well as those of a (theoretical) kaolinite transmission spectrum (Figure 3, blue and yellow spectra, respectively). Even though the quartz/clay sandstone contains only one weight percent of a very fine grained kaolinite (<10 μm; Rost et al., 2018), the kaolinite significantly contributes to the shape of the transmission spectrum, as is shown in Figure 3 (blue spectrum).

3.3. SEM Images

The scanning electron microscopy (SEM) images were obtained from the same surfaces of the pure quartz sandstone and the quartz/clay sandstone as the scanning electron microscopy (SEM) images presented in Rost et al. (2018). However, for this paper, the surfaces were chromium coated which resulted in higher resolution images that allowed to observe any clinging fines. The images are obtained with a high-efficiency secondary electron detector (HSE-SE2) from a Zeiss Merlin high resolution scanning electron microscope (HR-SEM; MESA+, University of Twente), with a maximum point resolution of 1.2 nm at 30 kV.

The polished surface of the pure quartz sandstone (Figure 4a) displays a smooth surface that is interrupted by pores and cavities of 100–200 μm in diameter and smaller cracks and pores of <10 μm in size. The sawed surface (Figure 4b) is rougher and also contains pores and cavities of 100–200 μm diameter. It shows that the grain fabric was strong enough to hold together while the saw blade cut through the quartz grains. A zoom-in of the sawed surface (Figure 4d) shows that sawing severely fractured the grain surfaces, generating fine-grained quartz fragments (as fine as a few microns in diameter), known as “clinging fines” (Wald & Salisbury, 1995). The split surface (Figure 4c) shows a distinct micro-topography along the edges of the subhedral to euhedral quartz grains. Estimated by masking and calculating the surface percentage from the SEM images there are ~20% intergranular cavities between the quartz grains, which is significantly more than the porosity of 6% reported by the supplier.
The grains at the individual surfaces of the split sample are predominantly smooth and straight due to their euhedral character.

The surfaces of the quartz/clay sandstone are not as smooth as the surfaces of the pure quartz sandstone (Figure 5). The SEM images show a sandstone with subhedral quartz with a grain size of ~250 μm and intergranular fine-grained (<10 μm) kaolinite and quartz minerals. The polished surface (Figure 5a) shows a partially smooth finish, but due to the higher porosity of this sample (20%; Reyer & Philipp, 2014), significant parts of the surface have not been polished. The sawed surface (Figure 5b) contains some cut grains but overall its surface is rougher than the sawed surface of the pure quartz sandstone. In addition, here are more small particles and chips. The split surface (Figure 5c) shows large grains that are less euhedral in their habitus than those of the pure quartz sandstone sample. The dominant grain surface is rough, with various rugged edges and dents. The zoom-in (Figure 5d) shows large patches of fine-grained kaolinite accumulates <10 μm grain size) that coat the cavities between the coarse-grained quartz, which can be seen on all three surfaces.

3.4. Description of the Non-Linear Spectral Model

We present a simple non-linear model that assumes that clinging fines (partly) blanket a rock surface, forming an optically thin layer that is penetrated by incoming light. The choice of this model was motivated by (Salisbury et al., 1994 page 11’904) who wrote:

“From these reflectance measurements, we believe that we have demonstrated that the spectral behaviour of our soil samples […] can be explained in essence by reflectance from an optically thick quartz substrate combined with transmission through very fine grained, optically thin, particulate coatings of kaolinite mixed with varying amounts of similarly fine quartz.”
Figure 4. Scanning electron microscopy images of the pure quartz sandstone surfaces. The polished surface is a smooth surface interrupted by large and small pores and cavities (C and c). The sawed surface is rougher and contains more pores (C). A zoom-in of the sawed surface shows fine-grained quartz fragments known as clinging fines (<10 μm, f) attached to the surface of larger grains. The split surface has a much more distinct micro-topography with large quartz minerals (G) that can have natural crystal planes (N), alternated with pores and cavities (C). Some of the mineral surfaces of the split surface are rougher, but not nearly as rough as the sawed surface.

Figure 5. Scanning electron microscopy images of the quartz/clay sandstone surfaces show that the surfaces of this sample are less smooth. The polished surface contains some smooth surfaces (P) that are alternated by pores and cavities (C), but a significant part of the surface has not been polished due to the higher porosity. The sawed surface shows some irregular quartz grains that occasionally have been sawed (S) and some fine-grained fragments between grains and attached to their surface (f). The split surface shows large quartz grains (G) that can be significantly rougher, or smoother than the sawed surface as a result of a natural mineral surface. The zoom-in shows large patches of fine-grained kaolinite accumulates (<10 μm, K) that fill up the cavities between the coarser grains and can be seen on all three surfaces.
The novelty of this model is that, instead of modeling the shape of individual particles and their interaction with incoming light, we compile components of the most common situations that light could encounter when interacting with a rock surface. We estimate the contribution of each component to the spectra by applying non-linear inversion to five unknown parameters which allows us to model the spectral shape variations in the reststrahlen features that we observed for the sawed and the split sample surfaces of the pure quartz sandstone and quartz/clay sandstone respectively (Rost et al., 2018).

In simple terms the model combines two (pure quartz sandstone) or three (quartz/clay sandstone) component spectra to model the measured reflectance spectrum of the rock samples. These components encompass the different combinations of clinging fines on the main mineral surface encountered by the reflected light.

The effect of multiplying the quartz reflectance by its transmission is to attenuate the longer wavelength components of the main reststrahlen feature more than the shorter wavelength components. Reflectance maxima in strong absorbers such as quartz are displaced to shorter wavelengths. This is the result of anomalous dispersion of the real part of the refractive index (Hapke, 1993; Section 4.5).

For our two samples, we identify the following components (Figure 6):

1. **Pure quartz sandstone**
   a) Optically thick quartz, resulting in a quartz reflectance spectrum.
   b) Optically thin quartz on quartz, resulting in a quartz transmission spectrum that superimposes onto a quartz reflectance spectrum.

3. **Quartz/clay sandstone**
   a) Optically thick quartz, resulting in a quartz reflectance spectrum.
   b) Optically thin quartz on quartz, resulting in a quartz transmission spectrum that superimposes onto a quartz reflectance spectrum.
   c) Optically thin kaolinite on quartz, resulting in a kaolinite transmission spectrum that superimposes onto a quartz reflectance spectrum.

The three listed components (Figures 6a–6c) are those that we conceptually consider necessary to model the pure quartz sandstone, and quartz/clay sandstone with a small percentage of kaolinite that we use in this study. More complex combinations of clinging fines (e.g., optically thin kaolinite on kaolinite) and influence of rock surface geometry (e.g., cavity effect) are not considered in this study, since this would make the model too complex.

### 3.4.1. Pure Quartz Sandstone

The equation for modeled reflectance of the pure quartz sandstone is:

\[
\rho = w_q \rho_q + w_{qq} \rho_q T_q
\]

where

- \( \rho \) is the modeled reflectance of the pure quartz sandstone sample.
- \( w_q \) is the fraction of optically thick quartz at the surface.
- \( \rho_q \) is the quartz reflectance spectrum.
- \( w_{qq} \) is the fraction of the surface that is quartz with a coating of optically thin quartz.
- \( T_q \) is the transmission spectrum of optically thin quartz with unknown thickness.

The transmission \( T_q \) depends on the physical thickness of the optically thin particles and is, as a result, sample dependent. We therefore parametrize the thickness of the optically thin quartz relative to a input transmission spectrum so that:
\[ T_q = \tau_q^{d_q} \]  

where \( \tau_q \) is the quartz input transmission spectrum and \( d_q \) is the unknown relative optical depth with respect to that input spectrum. For example, if \( d_q = 2 \), the thin quartz coating of the modeled sample has twice the optical thickness of the input transmission measurement for quartz.

### 3.4.2. Quartz/Clay Sandstone

To model the reflectance of the quartz/clay sandstone (with kaolinite), we add an additional term to Equation 1 for reflection after passing through thin kaolinite (Figure 6c).

The equation for modeled reflectance of the quartz/clay sandstone is:

\[ \rho = w_q \rho_q + w_{qq} \rho_q \tau_q + w_{qk} \rho_q \tau_k \]  

where 

- \( \rho \) is the modeled reflectance of the quartz/clay sandstone sample.
- \( w_q \) is the fraction of optically thick quartz at the surface.
- \( \rho_q \) is the quartz reflectance spectrum.
- \( w_{qq} \) is the fraction of the surface that is quartz with a coating of optically thin quartz.
- \( \tau_q \) is the transmission spectrum of optically thin quartz with an unknown thickness.
- \( w_{qk} \) is the fraction of the surface that is quartz with a coating of optically thin kaolinite.
- \( \tau_k \) is the transmission spectrum of optically thin kaolinite with an unknown thickness.

Both transmission terms depend on the physical thickness of the optically thin particles in relation to the input transmission spectra, and can be expressed as:

\[ T_q = \tau_q^{d_q} \quad \text{and} \quad T_k = \tau_k^{d_k} \]  

where \( \tau_q \) and \( \tau_k \) are the quartz and kaolinite input transmission spectra and \( d_q \) and \( d_k \) are unknown relative optical depths with respect to the input spectra.

### 3.4.3. Final Equations and Model Inversion

Substituting Equation 2 in Equation 1 and Equation 4 in Equation 3 gives reflectance of pure quartz sandstone (Equation 5) and quartz/clay sandstone (Equation 6) as:

\[ \rho = w_q \rho_q + w_{qq} \rho_q \tau_q^{d_q} \]  

and

\[ \rho = w_q \rho_q + w_{qq} \rho_q \tau_q^{d_q} + w_{qk} \rho_q \tau_k^{d_k} \]  

Thus the modeled spectrum of the radiation reflected from:

- normal (optically thick) quartz is (Figure 6a) \( w_q \rho_q \)
- quartz seen through optically thin quartz is (Figure 6b) \( w_{qq} \rho_q \tau_q^{d_q} \)
- quartz seen through optically thin kaolinite is (Figure 6c) \( w_{qk} \rho_q \tau_k^{d_k} \)

Table 1 shows the origin of the spectra that were used for the reflectance and transmission terms in Equation 5 and Equation 6. For our input quartz reflectance spectrum (\( \rho_q \)) we used the directional-hemispherical reflectance (DHR) spectrum of the polished pure quartz sandstone from Rost et al. (2018, Figure 2a). We assumed this spectrum of the polished surface to be unaltered by transmission. For the input quartz transmission spectrum (\( \tau_q \)) we used an attenuated total reflectance (ATR) transmission spectrum measured on a powder of the same rock (pure quartz sandstone). For the input kaolinite transmission spectrum, we used a mineral transmission spectrum of kaolinite calculated from Glotch et al. (2007). The measured rock spectra (\( \rho \)) that are to be modeled were
measured with directional-hemispherical reflectance (DHR) on two sample surfaces (sawed and split) of the two sandstones.

The unknown scalars \((w_q, w_{qq}, d_q, w_{qk}, d_k)\) were estimated by non-linear inversion using the CONSTRANDED_MIN procedure available in the programming language IDL (Interactive data language; Lasdon et al., 1978). This procedure minimizes the sum of squares of residuals between a modeled spectrum and a measured spectrum. Wavelength dependent weights are used to make the model more sensitive to residuals between 8.2 and 9.5 μm to allow for accurate modeling of the quartz reststrahlen doublet. When a model is perfect, the fractions calculated for pure quartz sandstone \((w_q \text{ and } w_{qq})\) and quartz/clay sandstone \((w_q' \text{ and } w_{qq}')\) per sample add up to a total of 1.0. We, however, have not constrained these parameters to unity because the main objective of our model is to accurately model the targeted spectra, regardless the calculated fractions.

4. Results

4.1. Modeling the Pure Quartz Sandstone

Figures 7a and 7b show the input quartz transmission spectrum \((T_q, \text{ dark purple})\) and its transformed version \((T_q \equiv \tau_q^{d_q}, \text{ magenta})\) for the sawed and split surfaces, respectively. The transmission spectrum \((T_q)\) of the sawed surface is low over large parts of its spectral range, specifically for the spectral range of the quartz reststrahlen doublet (8–10 μm). The split surface of the pure quartz sandstone (Figure 7b) has a higher transmission \((\tau_q)\) over the entire wavelength range as a result of the lower value of optical thickness \(d_q\). In Table 2, the weights calculated by the model show that, for the sawed surface, the contribution of optically thick quartz is significantly larger than that for quartz seen through optically thin quartz. For the split surface, there is no contribution from optically thick quartz suggesting that the sample spectrum can be modeled as only quartz seen through optically thin quartz.

Figures 7c and 7d compare the spectra of the measured pure quartz sandstone reflectance spectra of the sawed and split split spectrum respectively \((\rho, \text{ black})\) to the quartz input reflectance spectrum \((\rho_q, \text{ gray})\), the calculated spectra of the model components \((w_q \rho_q, \text{ dark blue })\) and \(w_{qq} \rho_q \tau_q^{d_q}, \text{ light blue })\) and the final modeled spectra \((w_q \rho_q + w_{qq} \rho_q \tau_q^{d_q}, \text{ red})\). Figure 7c shows an extreme example of reflectance attenuation at long wavelengths. For the sawed surface, the quartz seen through optically thin quartz \((w_{qq} \rho_q \tau_q^{d_q}, \text{ light blue})\) contributes a small peak with an amplitude of 0.04 that models the “horn” at 8.2 μm of the left lobe of the quartz reststrahlen doublet. This results in a response with a larger amplitude, that is just a scaled version of the normal quartz reflectance spectrum \((\rho_q, \text{ gray})\). The model also reproduces the variation in spectral contrast and the shape of the right lobe of the main reststrahlen features.

For the split surface (Figure 7d), no optically thick quartz is included in the fit and the spectrum is modeled solely as quartz seen through optically thin quartz \((w_{qq} \rho_q \tau_q^{d_q}, \text{ light blue})\). However, with an optical thickness \(d_q\) of only 0.27, the attenuation from optically thin quartz in the split surface is 99% less than the \(d_q\) of the sawed surface. This low value is to accommodate a lower amplitude of the long wavelength lobe of the quartz reststrahlen features.
feature while keeping amplitude of the short wavelength lobe constant. Overall, the model matches the spectrum of the split surface, but there is a slight discrepancy in the shape of the left lobe of the reststrahlen doublet where the model displays a bit of a horn feature which is not reflected in the measured spectrum. In addition, there is some deviation at the top of the right lobe of the reststrahlen feature.
Table 2
Scalars Estimated by the Model With Non-Linear Inversion to Determine the Fractions of Optically Thick Quartz ($w_{q}$), Quartz Seen Through Optically Thin Quartz ($w_{qq}$), Quartz Seen Through Optically Thin Kaolinite ($w_{qk}$), the Quartz Coating Thickness ($d_{q}$) and the Kaolinite Coating Thickness ($d_{k}$).

|                      | $w_{q}$ | $w_{qq}$ | $d_{q}$ | $w_{qk}$ | $d_{k}$ |
|----------------------|---------|----------|---------|----------|---------|
| Pure quartz sandstone sawed | 0.78    | 0.19     | 34.60   |          |         |
| Pure quartz sandstone split    | 0.00    | 0.95     | 0.27    |          |         |
| Quartz/clay sandstone sawed   | 0.82    | 0.43     | 40.57   | 0.00     | N/A     |
| Quartz/clay sandstone split   | 0.41    | 0.22     | 33.52   | 0.31     | 0.10    |

4.2. Modeling the Quartz/Clay Sandstone

Figures 8a and 8b show the transformed transmission spectra ($T_q = r_q^{d_q}$, magenta and $T_k = r_k^{d_k}$, yellow) for the sawed and split surfaces, respectively. The quartz transmission spectrum ($T_q$, magenta) of the sawed surface is low for large parts of its spectral range, specifically for the range of the quartz reststrahlen doublet (8–10 μm). The kaolinite transmission spectrum ($T_k$, yellow) is high (>0.85) over the entire range. Both surfaces show a high $d_q$ value of 40.57 and 33.52, responding to the presence of “horn” features in the measured spectra. The calculated weight of the sawed surface (Table 2) show that the contribution of optically thick quartz is about twice as large as the contribution of quartz seen through optically thin quartz. Also, no contribution of quartz seen through optically thin kaolinite is calculated. For the split surface, the contribution of optically thick quartz and quartz seen through optically thin quartz is half as much (50%) of what was calculated for these components for the sawed surface. This is compensated by a significant contribution of quartz seen through optically thin kaolinite.

Figures 8c and 8d compare the spectra of the measured quartz/clay sandstone reflectance spectra of the sawed and split surfaces respectively ($ρ$, black) to the quartz input reflectance spectrum ($ρ_q$, gray), the calculated spectra of the model components ($w_{q}ρ_q$, dark blue, $w_{qq}ρ_qT_q$, light blue and $w_{qk}ρ_kT_k$, green) and the final modeled spectra ($w_{q}ρ_q + w_{qq}ρ_qT_q + w_{qk}ρ_kT_k$, red). Figure 8c shows that, for the sawed surface, there is a quartz reststrahlen doublet with an amplitude of 0.44 for the optically thick quartz ($w_{q}ρ_q$, dark blue), a small peak with an amplitude of 0.06 for transmission through quartz ($w_{qq}ρ_qT_q$, light blue) and no kaolinite transmission effects modeled. The “horn” feature at 8.2 μm of the left lobe of the quartz reststrahlen doublet, as well as the shape of the right lobe in the measured spectrum are accurately reproduced by the model. However, the right lobe does not precisely match the peak position of the sample spectrum ($ρ$, black). In this case, the two quartz-related weights ($w_{q}$ and $w_{qq}$) sum to 1.25, the only instance where the sum of the weights does not approximate 1.0.

Figure 8d shows that, for the split surface, there is a quartz reststrahlen doublet with an amplitude of 0.23 for the optically thick quartz ($w_{q}ρ_q$, dark blue), a small peak with an amplitude of 0.03 for quartz seen through optically thin quartz ($w_{qq}ρ_qT_q$, light blue) and a distorted quartz reststrahlen pattern for the quartz seen through optically thin kaolinite ($w_{qk}ρ_kT_k$, green). Hence, all three components make substantial contributions for the final model ($w_{q}ρ_q + w_{qq}ρ_qT_q + w_{qk}ρ_kT_k$, red).

5. Discussion

This research is designed to better understand the physical processes that affect the shape and amplitude of reflectance spectra as a result from different rock sample preparation methods (i.e., polish, saw or split) and an accompanying difference in surface roughness. With our novel nonlinear model, we implemented an approach that compiles different combinations of optically thin mineral transmission on top of optically thick mineral reflectance spectra. To achieve this, the model combines optically thick quartz with transmission through (a) quartz clinging fines for the pure quartz sandstone and (b) quartz and kaolinite clinging fines for the quartz/clay sandstone.

Our nonlinear model reproduces the spectral amplitude and shape of the principal quartz reststrahlen doublet for three of the four sandstone spectra. In the three success cases, the nonlinear model allows to model spectral features of the reststrahlen doublet that are linked to transmission in quartz and kaolinite respectively (Salisbury et al., 1994): the “horn” feature of the left lobe (8.2 μm, Figure 7c) and the small spectral nick in the right lobe of the quartz reststrahlen doublet (9 μm; Figure 8d). The low transmission over most of the spectral range for the sawed surface of the pure quartz sandstone (Figure 7a) is a result of the high optical thickness $d_q$ of 34.60 that is calculated. For the quartz/clay sandstone the kaolinite transmission ($d_k$) is only calculated for the split surface, while for the sawed surface no transmission through optically thin kaolinite is included in the fit ($d_k = N/A$). For the split surface of the pure quartz sandstone, the model shows a discrepancy in the shape of the left lobe of the quartz reststrahlen doublet; the model has a horn feature and a slight deviation of the top of the right lobe of the
Figure 8. Input and calculated spectra of the quartz/clay sandstone model. (a) shows the transformed quartz transmission spectrum $T_q = \tau_q^A$ (magenta) for the sawed sample surface. No transformed kaolinite transmission was calculated because the model did not calculate any optical thickness for kaolinite (Table 2, $d_k = \text{N/A}$). (b) shows transformed quartz transmission spectrum $T_q = \tau_q^A$ (magenta) for the split sample surface and the transformed kaolinite transmission spectrum $T_k = \tau_k^A$ (yellow). Note that the transformed quartz spectra are almost identical because they both have a high optical thickness (Table 2). (c) shows the final model results for the sawed surface ($w_q \rho_q + w_{qq} \rho_q T_q + w_{qk} \rho_k T_k$, red) compared to the measured rock spectrum ($\rho$, black), including the quartz input reflectance spectrum ($\rho_q$, gray). The model combines optically thick quartz reflectance ($w_q \rho_q$, dark blue) with reflectance through optically thin quartz ($w_{qq} \rho_q T_q$, light blue), but does not incorporate any reflectance through optically thin kaolinite in the model. (d) shows the final model results for the split surface ($w_q \rho_q + w_{qq} \rho_q T_q + w_{qk} \rho_k T_k$, red) compared to the measured rock spectrum ($\rho$, black). The model combines optically thick quartz reflectance ($w_q \rho_q$, dark blue) with reflectance through optically thin quartz ($w_{qq} \rho_q T_q$, light blue) and reflectance through optically thin kaolinite ($w_{qk} \rho_k T_k$, green).
reststrahlen feature compared to the sample spectrum. The implications of these deviations is discussed below in the model limitations section.

The nonlinear model helps to identify the underlying physical process on how a different surface roughness causes differences in spectral amplitude and shape. It confirms the theory of Salisbury et al. (1994) that the spectral shape of the “horn” feature in the left lobe (8.2 μm; Figure 7c) and the small spectral nick in the right lobe of the quartz reststrahlen doublet (9 μm; Figure 8d) result from transmission in quartz and kaolinite clinging fines, respectively. Other causes such as the cavity effect or multiple surface reflections, as suggested by Rost et al. (2018), are not necessary to model the spectral shape and amplitude. However, all other effects discussed in literature could still be operating in our data, but are absorbed by the variability of the model’s parameters. We merely show that the data can be explained by transmission effects alone. Furthermore, the nonlinear model correctly displays the strong bands of the quartz reststrahlen doublet (8–10 μm), which has proven too complex for emission-based models that only describe the effect of grain size and packing density of particles (Moersch & Christensen, 1995; Mustard & Hays, 1997).

The model also has limitations. The model for the split surface of the pure quartz sandstone incorrectly displays the peak position of the right lobe and a slight “horn” feature for the left lobe of the quartz reststrahlen doublet. This can be linked to a difference in peak position of the input reflectance spectrum (polished surface of the pure quartz sandstone) versus the spectrum of the split surface targeted by the model (Figure 2b). The model for the split surface of the pure quartz sandstone only incorporates the component of optically thick quartz seen through optically thin quartz, with a quartz coating that has a minimal optical depth of 0.27 (Table 2). Contrary to what we expected, the optically thick quartz component is not included. This results in a small “horn” feature at 8.2 μm that can be linked to transmission in quartz (Salisbury et al., 1994). To describe the right lobe of the reststrahlen doublet, the model incorporates quartz transmission to approximate the peak position of the split surface spectrum. Hence, the modeled split surface spectrum of the pure quartz sandstone shows that the shifts in peak position are integrated in the model influencing both the type of components selected by the model as well as the calculated weights. Whether the peak positions of the input spectra influence the model results, depends on the weights the model assigns to the spectra. Thus, in some cases, the features of the spectra used as input by the model will influence model results depending on both the extent of variation in peak position between the input spectrum and the targeted spectrum as well as the weights assigned to the spectra by the model.

For the sawed surface of the quartz/clay sandstone the two weights (w_q and w_k) add up to 1.25 instead of 1.0. The main focus of our model is the spectral fit of the data, the weights calculated to achieve this fit are secondary result which we use to quantify reliability of the fit. When the weights do not add up to unity there is probably an extra uncalibrated variable, like the cavity effect, that is scaling the whole spectrum with an unknown factor. The model does not incorporate any transmission from kaolinite (w_k) for the sawed surface of the quartz/clay sandstone while for the split surface, the model calculates a weight of 0.31 for quartz seen through kaolinite component (w_qk). This sandstone contains only 1% of kaolinite (Rost et al., 2018). The SEM images suggest that sawing did not expose kaolinite accumulates. Instead, it appears they were protected in between the quartz grains because the saw cut through the quartz grains. Therefore, the 1% kaolinite does not sufficiently influence the sawed surface spectrum and the model does not need to incorporate kaolinite. For the split surface, there are more kaolinite accumulates visible on the SEM images. We hypothesize that kaolinite became exposed when splitting the surface, because it is a weaker mineral than quartz. The sandstone is thus more likely to break along the kaolinite, resulting in an over-representation at a split surface. However, the SEM images do not support a value of 0.31 as estimated by the model. Nonetheless, we conclude that small shape variations in the spectra, resulting from as little as 1% of a certain mineral, are identified and incorporated by the model. Note however, that clay minerals often display noticeable spectral features, unlike other minerals. Therefore, identifying effects of other minerals could be more challenging.

The polished surface of the pure quartz sandstone is the source of the input reflectance spectrum. Our assumption is that its spectrum is not affected by transmission. We deem this assumption valid because we do not observe features in this spectrum that suggest transmission has occurred. Nonetheless, small percentages of transmission could have influenced the spectral contrast of the spectrum over its entire wavelength range, resulting in a lower amplitude of the spectrum. This could affect the reliability of the weights calculated by the model, however, for components that have distinct absorption features this effect will be minimal and, in such cases, the obtained weights are still valid.
We used only three components and chose to not include effects from other minerals in our model. We believe these three components are a realistic representation of the samples, since their composition is relatively well constrained with X-ray diffraction (Rost et al., 2018) and SEM imaging, therefore there are no indications there are other minerals present in the sandstones that have an effect on their spectral signature. Furthermore, we did not include a component with optically thick kaolinite. The SEM images of the kaolinite accumulates (Figure 5d) show that this thin, platy mineral forms stacks that can be up to 20 μm thick. This suggests that some accumulates are sufficiently thick to be classified as optically thick. However, the sandstone contains only 1% of kaolinite of which the vast majority are in those accumulates. We suspect that very little kaolinite is needed to cause the effects we see in the quartz spectra. Also, we can adequately model the spectra without a optically thick kaolinite component. Therefore, we choose to not include it.

The valuable insight gained from this work can be used to compile a model that incorporates both the traditional particle scattering and RT hybrid models and our novel nonlinear component model. For particles or surface coatings larger than the wavelength (geometric optics regime, $D \gg \lambda$; Hapke, 1993), hybrid models like Mie/Hapke and MSTM/Hapke can be used, that start from optical constants and worked reasonably well for this scattering regime (Arnold, 2014; Ito et al., 2017; Mustard & Gloitch, 2019). When modeling fine particles or surface coatings smaller than the wavelength (Rayleigh scattering, $D \ll \lambda$; Hapke, 1993) our nonlinear component model can be applied. This would result in a new hybrid model that encompasses all scattering regimes from coarse to fine grained particles including clinging fines coating rock surfaces.

However, our model was tested on rock samples that have a limited number of minerals. Using it for mineralogically more complex samples would be challenging as it becomes difficult to assign spectral features that result from transmission to a specific mineral. Complex samples will increase the number of mineral components, individual components and spectral complexity of the model results. Therefore, additional constrains on component composition and model weights might be necessary.

Another innovation would be to use model results to correct for transmission effects that occur in a spectrum, by subtracting transmission components of the model. When a spectrum contains features that suggest effects from transmission, the model can calculate the transmission components (in the case of our sandstones $u_{\text{qf}}\rho_f\tau_{\text{qf}}$ and $u_{\text{kf}}\rho_f\tau_{\text{kf}}$) and subtract these spectra from the measured spectrum. The result is a spectrum that is unaltered by transmission and supposedly unaffected by surface roughness, except surface roughness also affects the number of surface cavities which are approximately linearly related to a decrease in spectral contrast (Kirkland et al., 2003). Therefore the cavity effect should also be taken into account.

Additionally, a possible complexing factor would be that eliminating the effect of transmission through clinging fines could also influence amplitude of the spectral features linked to that mineral and, consequently, the interpretation of the mineralogical composition. Therefore, future research on spectral correction of transmission effects should also take into account the effect of correction on the spectral amplitude and the interpretation of the mineralogical composition.

### 6. Conclusions

This research improves the understanding of the physical processes that influence the relationship between the surface roughness of rocks and the spectral shape and amplitude of thermal infrared spectra. With the nonlinear model, we implemented a novel approach that compiles different combinations of optically thin mineral transmission on top of optically thick mineral reflectance spectra. To achieve this, the model combines optically thick quartz with transmission through quartz and kaolinite clinging fines.

Our nonlinear model reproduces spectral amplitude and shape of the principal quartz reststrahlen doublet of three of the four sandstone spectra. It also correctly displays the strong bands of the quartz reststrahlen doublet, which proved challenging for previous models (Arnold, 2014; Hardgrove et al., 2016; Ito et al., 2017; Mackowski & Mishchenko, 2011; Moersch & Christensen, 1995; Mustard & Hays, 1997; Pitman et al., 2005; Wald & Salisbury, 1995).

The results confirm the theory of Salisbury et al. (1994) that spectral shape changes observed in the reststrahlen doublet of the spectra result from transmission in quartz and kaolinite clinging fines (Salisbury et al., 1994). Other causes such as the cavity effect or multiple surface reflections, as suggested by Rost et al. (2018), are not
necessary to model the spectral shape and amplitude. However, all other effects discussed in literature could still be operating in our data, we merely show that the data can be explained by transmission effects alone. For the split surface of the pure quartz sandstone, the model integrates shifts in peak position, influencing both the type of components selected by the model as well as the calculated weights. Showing that, in some cases, our model is not successful and spectral features of the input spectra impact model results, especially the calculated weights of the components. Nonetheless, the results show that reflectance and transmission based modeling is a promising technique for identification and correction of spectral characteristics that result from a different surface roughness.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The reflectance and transmission spectra, model results, Interactive data language scripts and scanning electron microscopy images presented in this paper can be found at https://zenodo.org/record/5647403#KUK (Rost & Green, 2021; https://doi.org/10.5281/zenodo.5647403). The reflectance spectra presented in this paper are available through Rost et al., 2018 and can be found at https://easy.dans.knaw.nl/ui/datasets/id/easy-dataset:158377 (https://doi.org/10.17026/dans-xzt-e99). The IGSN identifiers for samples used for this research are IE7/90001 and IE7/790003.

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