Spectral properties of angrites

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Abstract–Angrites are generally believed to be fragments of a basaltic asteroid that differentiated under relatively oxidizing conditions. Almost all angrites (e.g., D'Orbigny, Lewis Cliff [LEW] 86010, and Sahara 99555) are composed predominately of anorthite, Al-Ti diopside-hedenbergite, and Ca-rich olivine, except for the type specimen, Angra dos Reis, which is composed almost entirely of Al-Ti diopside-hedenbergite. D'Orbigny, LEW 86010, and Sahara 99555 also have spectral properties very different from Angra dos Reis. These newly measured angrites all have broad absorption features centered near 1 μm with very weak to absent absorption bands at ~2 μm, which is characteristic of some clinopyroxenes. The spectrum of Angra dos Reis has the characteristic 1 and 2 μm features due to pyroxene. One asteroid, 3819 Robinson, has similar spectral properties to the newly measured angrites in the visible wavelength region, but does not appear to spectrally match these angrites in the near-infrared.

INTRODUCTION

Meteorites believed to be asteroidal basalts (e.g., angrites or eucrites) provide unique insights into planetary differentiation because of their formation during partial melting and melt migration and our ability to compare them to the extensive body of literature on terrestrial basalts. These rocks, which are rich in calcium-rich plagioclase feldspar and augitic pyroxene, crystallized from near-surface intrusive and extrusive magma bodies. Among meteoritic basalts, eucrites are the best known and understood. Along with howardites and diogenites, they comprise a series of partial melts (eucrites), crystal cumulates (orthopyroxene-rich diogenites), and polymict breccias (howardites), exhibiting continuous variations in mineralogy and mineral chemistry and are thought to originate from the crust of a common asteroidal body. Spectral reflectance data and dynamic modeling link the howardites, eucrites, and diogenites (HEDs) to the ~500 km-diameter asteroid 4 Vesta (McCord et al. 1970) through small, Vesta-like objects (vestoids) (Binzel and Xu 1993; Burbine et al. 2001b; Kelley et al. 2003). These vestoids link Vesta to the meteorite-delivering 3:1 resonance and could be impact-derived fragments from a polar basin on Vesta (Thomas et al. 1997).

Other meteorites are petrologically similar to the eucrites, but differ either in oxygen isotopic composition (Ibitira [Mittlefehldt 2005], NWA 011 [Yamaguchi et al. 2002]), or trace element chemistry (mesosiderites [Mittlefehldt et al. 1998]) and appear to have been derived from similar but distinct parent bodies. This recognition of samples from additional parent bodies is accompanied by a recognition of new, basalt-like asteroids in the Main Belt, including 1459 Magnya (Lazzaro et al. 2000; Harderson et al. 2004) and a number of S-type asteroids including 17 Thetis and members of the Merxia and Agnia families (Sunshine et al. 2004). Even with these additional meteorite and potential parent asteroids, the number of basaltic parent bodies pales in comparison to the number of differentiated bodies inferred from studies of iron meteorites (about 50–70 differentiated asteroid-sized parent bodies) (Wasson 1995; Burbine et al. 2002).

The angrites are a group of meteorites for which a basalt-covered parent body is likely required, although alternative views have been voiced by Kurat et al. (2004), Jambon et al. (2005), and Varela et al. (2005). The angrites are composed predominantly of anorthite, Al-Ti diopside-hedenbergite, and Ca-rich olivine (including sub-calcic kirschsteinite) (Mittlefehldt et al. 2002). Oxygen isotopic measurements (Greenwood et al. 2005) are consistent with all measured angrites originating from the same parent body or from the same oxygen isotopic reservoir. Angrites are particularly
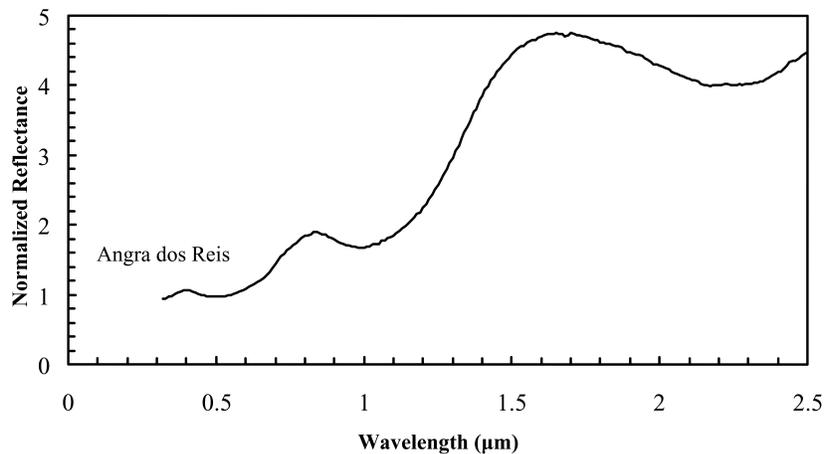
Fig. 1. A reflectance spectrum of Angra dos Reis. The spectrum is normalized to unity at 0.55 μm.

intriguing because their mineralogy, which differs so dramatically from eucrites, reflects formation under markedly different oxygen fugacities. Jurewicz et al. (1991, 1993) found that partial melts of carbonaceous chondritic material resembled either angrites or eucrites, depending on the oxygen fugacity during melting. Relatively oxidizing conditions produced partial melts similar to angrites while relatively reducing conditions produced partial melts similar to eucrites.

The identification of angritic parent bodies would possibly allow oxygen fugacity conditions to be mapped in the asteroid belt. Linking angrites with any asteroids was previously hampered by the fact that the first discovered angrite, Angra dos Reis, had a spectrum (Gaffey 1976) unlike any known asteroid. The spectrum of Angra dos Reis is extremely reddened (reflectance increasing with increasing wavelength) with very distinctive pyroxene absorption bands (Fig. 1). Even though it is the type specimen, Angra dos Reis is compositionally anomalous compared to other angrites since it is composed almost entirely of Al-Ti diopside-hedenbergite with only rare plagioclase (Prinz et al. 1977). It is generally believed that Angra dos Reis formed as a cumulate (e.g., Prinz et al. 1977).

Recently, the discoveries of two relatively large angrites (D'Orbigny and Sahara 99555) have allowed for the measurement of the spectral properties of meteorites that may be more typical of the surface compositions of the angritic parent bodies. This paper discusses the spectral properties of Angra dos Reis, D'Orbigny, and Sahara 99555 plus one Antarctic angrite (Lewis Cliff [LEW] 86010, the second angrite discovered) and possible parent bodies.

SAMPLES AND TECHNIQUES

Room temperature reflectance spectra for Angra dos Reis (RELAB Sample ID TB-TJM-119), D'Orbigny (TB-TJM-062), LEW 86010 (MT-TJM-010), and Sahara 99555 (TB-

TJM-057) were obtained using the bidirectional spectrometer at the Keck/NASA reflectance experiment laboratory (RELAB) facility (http://www.planetary.brown.edu/relab/index.html) located at Brown University. Except for Angra dos Reis, these samples were ground with a mortar and pestle and sieved to particle sizes less than 125 μm for D'Orbigny and Sahara 99555 samples, and less than 74 μm for the LEW 86010 sample. The Angra dos Reis sample was ground to a powder, but not sieved due to the small amount of sample available. The Angra dos Reis and D'Orbigny samples were supplied by Gero Kurat at the Naturhistorisches Museum, the LEW 86010 sample was supplied by the Meteorite Working Group, and the Sahara 99555 sample was supplied by Arthur Ehlmann at Texas Christian University.

Low-temperature spectra of D'Orbigny were acquired at the Planetary Geosciences/HIGP (Hawai'i Institute of Geophysics and Planetology) spectrometer facility at the University of Hawai'i at Manoa (e.g., Hinrichs and Lucey 2002). This D'Orbigny sample was from the Smithsonian collection and was initially part of a sample that was scanned using X-ray computed tomography (McCoy et al. 2002). For this spectrometer, the incident and emission angles were both 10.5°. The spectral coverage was ~0.36 to 2.5 μm with a sampling interval of 0.001 μm. The usable temperature range was ~120 K to 240 K at 20 K intervals plus a measurement at approximately room temperature (300 K).

The Angra dos Reis meteorite contains ~90% Al-Ti diopside-hedenbergite (Prinz et al. 1977) with minor Ca-rich olivine (including sub-calcic kirschsteinite). Plagioclase grains are very rare in Angra dos Reis. D'Orbigny and Sahara 99555 both contain approximately one-third anorthite, one-third Ca-rich olivine (including sub-calcic kirschsteinite), and 20–25% Al-Ti diopside-hedenbergite (Mikouchi et al. 2000a, 2000b; Mikouchi and McKay 2001; Mittlefehldt et al. 2002). Mittlefehldt et al. (2002) found that D'Orbigny is compositionally indistinguishable from Sahara 99555. Modal analyses of LEW 86010 by Delaney and Sutton (1988),
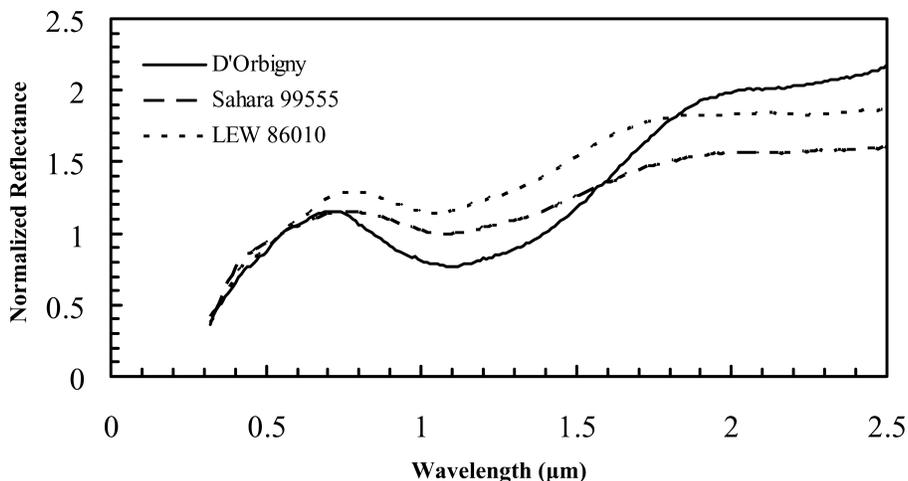
Fig. 2. Reflectance spectra of D'Orbigny, LEW 86010, and Sahara 99555 from RELAB. Spectra are normalized to unity at 0.55 μm.

Goodrich (1988), and Prinz et al. (1988) obtained abundances of ~20% anorthite, ~20% Ca-rich olivine (including sub-calcic kirschsteinite), and ~60% Al-Ti diopside-hedenbergite. Modal analyses of LEW 86010 by McKay et al. (1988) obtained lower abundances of Al-Ti diopside-hedenbergite (43%) and higher abundances of anorthite (32%) than the other analyses, which may imply some compositional heterogeneity in LEW 86010.

The pyroxenes in Angra dos Reis have an average composition of $\sim Fs_{12}Wo_{55}$ (Prinz et al. 1977) and tend to be very homogeneous in composition (Prinz et al. 1977). Pyroxene grains in D'Orbigny vary significantly in enstatite ($\sim En_{0-28}$) and ferrosilite ($\sim Fs_{20-49}$), but very little in wollastonite ($\sim Wo_{51-54}$) (Mittlefehldt et al. 2002) and tend to be zoned with the MgO concentration decreasing toward the rim. Pyroxene grains in Sahara 99555 (Mikouchi, personal communication) have similar compositions and similar zoning as D'Orbigny. Pyroxene grains in LEW 86010 ($En_{23-36}Fs_{13-20}Wo_{52-57}$) (Crozaz and McKay 1990; Mittlefehldt et al. 1998) also tend to be zoned (Goodrich 1988; Prinz et al. 1988; Mikouchi and McKay 2001).

RESULTS

The spectrum (Gaffey 1976; Mao et al. 1977) of Angra dos Reis has the distinctive absorption features centered at ~1 and ~2 μm due to pyroxene and is extremely red. The feature with a band minimum at ~0.5 μm is due to a Fe^{2+} to Ti^{4+} intervalence charge transfer transition (Mao et al. 1977; Burns 1993a).

The room-temperature reflectance spectra of D'Orbigny, LEW 86010, and Sahara 99555 all have similar spectral characteristics (Fig. 2). These meteorites all have broad absorption features centered near 1 μm and very weak to non-existent absorption bands centered at ~2 μm. This is in contrast to the strong 2 μm absorption band present in the Angra dos Reis spectrum. The spectra of D'Orbigny, LEW 86010, and Sahara 99555 are relatively red, but not as red as the Angra dos Reis spectrum. The albedos of these samples are also very different. D'Orbigny (reflectance is 0.14 at 0.55 μm), LEW 86010 (0.30), and Sahara 99555 (0.24) are much brighter than Angra dos Reis (0.04). However, the extremely low albedo of Angra dos Reis may be due to this samples having a larger grain size than the other angrites since the Angra dos Reis samples was not sieved.

In pyroxenes, cations occur in two different crystallographic sites called M1 and M2. The M2 site is larger and much more distorted than the M1 site. Fe^{2+} in the M2 site produces the characteristic 1 and 2 μm pyroxene absorption bands (e.g., Burns 1993a, 1993b). A number of cations (e.g., Ca, Na, Co, Zn, Cr, Mn) strongly partition into the M2 site due to their relatively large radii and any deficiencies in M2 site occupancy by these cations can be made up by Fe^{2+} (Cloutis et al. 2006).

The presence of a 1 μm band but a very weak to absent 2 μm feature is characteristic of some high-Ca pyroxenes (e.g., Adams 1975; Cloutis and Gaffey 1991; Schade et al. 2004) where Fe^{2+} is located almost entirely in the M1 site. These pyroxenes (called type A) have two absorption bands centered at ~0.90 and ~1.15 μm that partially overlap; however, the overlapping olivine absorption feature wipes out this structure in the angrite spectra. High-Ca pyroxenes with both 1 and 2 μm features are called Type B.

Cloutis and Gaffey (1991) found that pyroxenes with type A spectra had pyroxenes with wollastonite contents greater than 50%. But they also found that there was considerable overlap between these two spectral types of pyroxenes. Schade et al. (2004) found that clinopyroxenes with $Fs \geq 30$ and $Wo \geq 47$ had type A spectra. However, the pyroxene compositions in angrites fall outside the pyroxene quadrilateral due to high abundances of Al^{3+} and Ti^{4+} so using ferrosilite and wollastonite contents may not be the best way
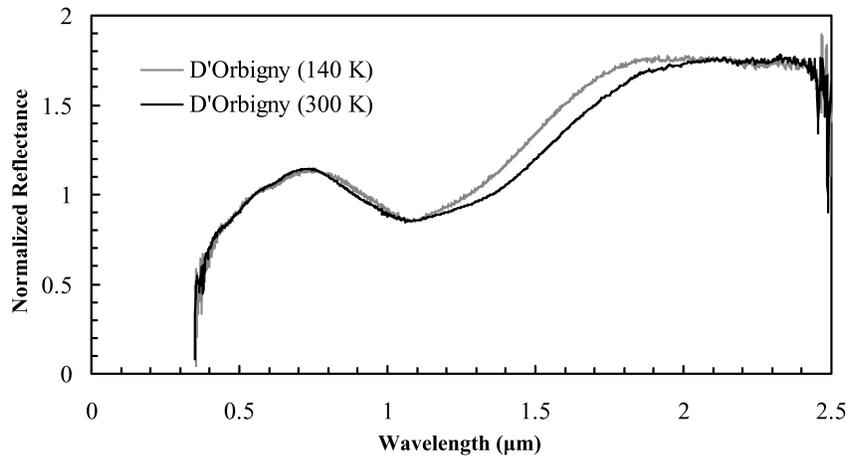
Fig. 3. Reflectance spectra of D'Orbigny at 140 K and 300 K from the University of Hawai'i. Spectra are normalized to unity at 0.55 µm.

to characterize these pyroxene compositions. Looking at calculated cation formulas (assuming six oxygens) for pyroxenes in these angrites (Mittlefehldt et al. 1998; Mittlefehldt et al. 2002; Mikouchi, personal communication), the number of Ca cations for pyroxenes in Angra dos Reis (0.967) is smaller than the average values calculated for D'Orbigny (0.975), LEW 86010 (0.992), and Sahara 99555 (0.985), which is consistent with type A pyroxenes having higher average calcium contents. But there is some variation in the calculated calcium contents of pyroxenes in these meteorites. For example, pyroxenes in D'Orbigny range in the number of calculated Ca cations from ~0.953 to ~0.993 (Mittlefehldt et al. 2002).

Schade et al. (2004) also found that other factors such as high Fe^{3+}/Fe^{2+} ratios and high concentrations of Mn in the pyroxenes could cause pyroxenes to have type A spectra. D'Orbigny and Sahara 99555 have both been found to contain some Fe^{3+} in their pyroxenes (Hoffman 2002), but the Fe^{3+}/Fe^{2+} ratios in these meteorites are very low (less than ~5% from Mössbauer analyses). The Mn concentrations in the D'Orbigny, LEW 86010, and Sahara 99555 pyroxenes (MnO of 0.09–0.24) (Crozaz and McKay 1990; Mittlefehldt et al. 1998; Mikouchi, personal communication) are only slightly higher than those in Angra dos Reis (MnO of 0.06 wt%).

Not much Fe^{2+} is needed in the M2 site to produce a significant 2 µm feature. From the structural formula for the diopside-hedenbergite in Angra dos Reis (Hazen and Finger 1977), 2% of the cations in the M2 site are Fe^{2+} while 21% of the cations in the M1 site are Fe^{2+}. The bands due to Fe^{2+} in the M2 site are much more intense than bands due to Fe^{2+} in the M1 site (e.g., Straub et al. 1991). So even though Fe^{2+} is concentrated in the M1 site, bands due to the Fe^{2+} in the M1 site will not be apparent unless there is little to no discernible Fe^{2+} in the M2 site. Cloutis et al. (2006) find that Angra dos Reis has a higher percentage of Fe^{2+} in the M2 site than D'Orbigny or LEW 86010, which is consistent with the spectral properties of these angrites.

So why does the diopside-hedenbergite in Angra dos Reis have a higher abundance of Fe^{2+} in the M2 site than the diopside-hedenbergite in D'Orbigny and Sahara 99555? The partition coefficient $[K_d = (Fe^{2+}/Mg)^{M1}/(Fe^{2+}/Mg)^{M2})]$ for Fe^{2+} and Mg between the M1 and M2 sites for clinopyroxenes tends to increase with increasing temperature (McCallister et al. 1976). So the scarcity of Fe^{2+} in the M2 site of diopside-hedenbergite in D'Orbigny, LEW 86010, and Sahara 99555 may indicate that these pyroxenes formed at higher temperatures than those in Angra dos Reis. The homogeneous nature of the pyroxenes in Angra dos Reis also indicates that the pyroxenes in this meteorite cooled relatively slowly while zoning of the pyroxenes in D'Orbigny, LEW 86010, and Sahara 99555 indicates that they cooled relatively quicker than the pyroxenes in Angra dos Reis. The quicker cooling rates of these three meteorites may not have allowed Fe^{2+} to have enough time to partition into the M2 site.

The spectra of D'Orbigny, LEW 86010, and Sahara 99555 are relatively red, but not as red as the Angra dos Reis spectrum (Fig. 2). These slope differences could be due to a number of factors including terrestrial weathering, differences in the spectral properties of type A and B clinopyroxenes, and the lower abundances of fassaite in D'Orbigny, LEW 86010, and Sahara 99555 compared to Angra dos Reis.

Low-temperature reflectance spectra of D'Orbigny were also obtained to understand how absorption features of angrites might change at the low temperatures (~140–200 K) that occur on asteroid surfaces in the main belt (Hinrichs et al. 1999). We plot reflectance spectra (Fig. 3) of D'Orbigny at 140 K and 300 K. As expected, the width of the 1 µm band shrinks with decreasing temperature. There is a decrease in band width of ~10% from room temperature to 140 K. The band width is derived by determining the distance from the peak at ~0.7 µm to a point with a similar reflectance value on the far side of the 1 µm feature.
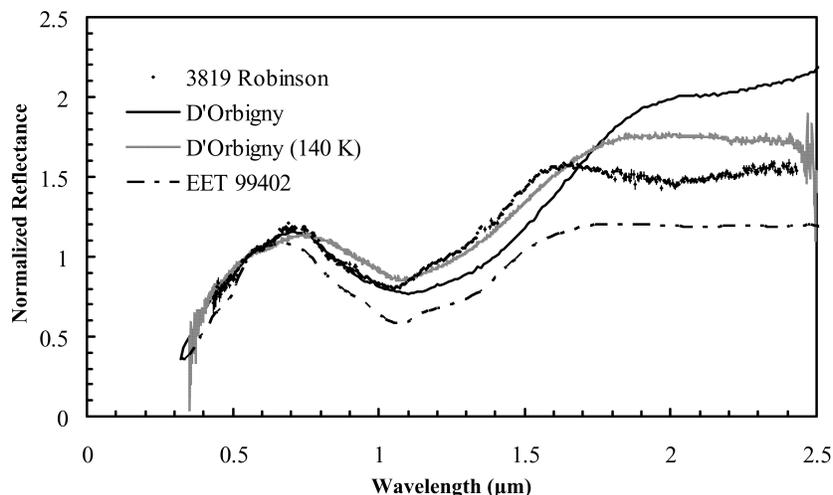
Fig. 4. Reflectance spectra of D'Orbigny at room temperature (RELAB) and 140 K (University of Hawai'i), and brachinite EET 99402 versus the spectrum of 3819 Robinson. The Robinson spectrum is a combination of visible data from Bus and Binzel (2002a) and Bus (unpublished data). The error bars for 3819 Robinson are one sigma. Spectra are normalized to unity at 0.55 μm.
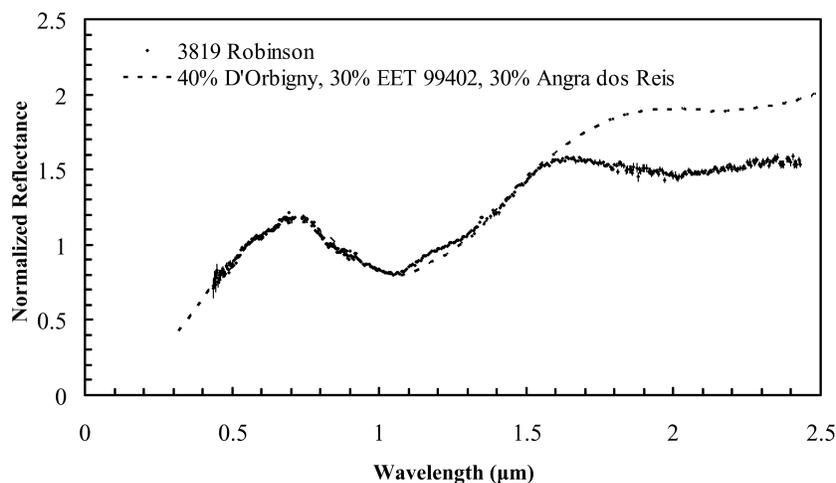

Fig. 5. Reflectance spectrum of a theoretical mixture of 40% D'Orbigny (RELAB), 30% EET 99402, and 30% Angra dos Reis versus the spectrum of 3819 Robinson. The theoretical mixture is a checkerboard model where the spectral properties of the meteorites are assumed to add linearly. The Robinson spectrum is a combination of visible data from Bus and Binzel (2002a) and Bus (unpublished data). The error bars for 3819 Robinson are one sigma. Spectra are normalized to unity at 0.55 μm.

ASTEROIDS

Currently, no asteroid has been found to be a spectral "match" to known angrites in both the visible and near-infrared wavelength regions. Hardersen et al. (2006) has proposed that S-type asteroid 138 Tolosa could possibly be a mixture of Type A and B pyroxenes, but this object does not appear spectrally similar to measured angrites. Cloutis et al. (2006) has investigated whether 3628 Božněmcová could be covered with angritic material. Asteroids classified as Sr in the Bus and Binzel (2002b) taxonomy, such as 3819 Robinson (semimajor axis of 2.77 AU), have spectra that match angrites very closely in the visible wavelength region (0.44 to 0.92 μm) (Fig. 4).

Asteroid 3819 Robinson was identified (Burbine et al. 2001a) as possibly having a similar surface composition to angrites from the analysis of near-infrared reflectance spectra taken out to 1.65 μm (Burbine and Binzel 2002). However, higher-resolution spectra (Bus, personal communication) taken using SpeX (Rayner et al. 2003) with wavelength coverage out to 2.5 μm shows some noticeable spectral differences between Robinson and angrites.

Robinson matches very well the visible portion of the RELAB D'Orbigny spectrum (Fig. 4). The band width of the 1 μm feature matches very well the width of the D'Orbigny spectrum taken at 140 K. However, the Robinson spectrum has a band minimum (1.05 μm) and band structure more similar to the olivine-rich brachinite EET 99402 (TB-TJM-

058) (particle size less than 125 μm) (band minimum at
1.07 μm) than D'Orbigny (band minimum at 1.08–1.10 μm).
Both Robinson and EET 99402 show a slight convex
curvature near ~1.20 μm and a slight concave curvature near
~1.25 μm, which is characteristic of olivine. Robinson also
has a weak 2 μm band, which is centered at a different in
wavelength position than D'Orbigny's weak 2 μm feature.
Robinson's reflectance spectrum appears more consistent
with an olivine-dominated composition (Sunshine, personal
communication) than an angritic surface.

To see if some mixture of angritic material (including
Angra dos Reis) and olivine could duplicate the Robinson
spectrum, theoretical mixtures of RELAB spectra of
D'Orbigny, EET 99402, and Angra dos Reis were produced.
A checkerboard model was assumed with the spectral
properties of the meteorites adding linearly. The "best" match
(Fig. 5) from 0.4 to 1.5 μm appears to be a mixture of 40%
D'Orbigny, 30% EET 99402, and 30% Angra dos Reis.
However, this mixture fails to match Robinson's slight
convex curvature near ~1.20 μm and slight concave curvature
near ~1.25 μm and the wavelength position of Robinson's
2 μm band.

CONCLUSIONS

Angrites D'Orbigny, LEW 86010, and Sahara 99555 all
have spectral properties very different from Angra dos Reis,
the first known angrite. These newly measured angrites all
have broad absorption features centered near 1 μm with very
weak to absent absorption bands at ~2 μm while Angra dos
Reis has the characteristic 1 and 2 μm features due to
pyroxene. Sr-asteroid 3819 Robinson has similar spectral
properties to the newly measured angrites in the visible
wavelength region, but does not appear to spectrally match
these angrites in the near-infrared.

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