Barite and Celestine Detection in the Thermal Infrared - Possible Application to Determination of Aqueous Environments on Mars. D. M. Burt[1], L. E. Kirkland[2,3], and P. M. Adams[3], [1]Arizona State University, DONALD.BURT@asu.edu; [2]Lunar and Planetary Institute, kirkland@lpi.usra.edu, [3]The Aerospace Corporation, paul.m.adams@aero.org. On-line information and data: www.lpi.usra.edu/science/kirkland

Introduction: Two minerals commonly cited as possible indicators of former aqueous environments on Mars are 1) calcite, calcium carbonate, as an indicator of calcium weathered from mafic igneous rocks reacting with carbon dioxide in the martian atmosphere, presumably in the presence of water, and 2) coarsely-crystalline or gray hematite (specularite, ferric iron oxide) as an indicator of former hydrothermal activity, which would promote the growth of larger than normal crystals (finely crystallized hematite has been proposed for hundreds of years as the cause of the red color of Mars). Problems with these approaches are 1) that the surface of weathered calcite can become pitted and rough, owing to its softness and relatively high solubility in water, thus making spectroscopic detection difficult [1], and 2) that finely crystallized hematite can occur as an extremely thin, shiny (specular) coating, whose spectrum closely matches that of the coarse-grained hematite [2]. Another, more general problem is that Ca and Fe are both extremely abundant in igneous rocks, so that calcite and hematite can form in the presence of not very much water, under a huge variety of conditions. These problems imply unavoidable ambiguity for claims involving either the detection or non-detection of the above minerals, and problems of interpretation even if they are detected unambiguously.

Here we suggest trying instead to look on Mars for two easily detected sulfate minerals, barite, $BaSO_4$, and celestine, $SrSO_4$, which indicate their respective aqueous environments (hydrothermal and evaporitic). The relatively low geochemical abundances of Ba and Sr in mafic igneous rocks, and the relatively low solubilities of barite and celestine in water, imply that a great deal of water is needed to form substantial deposits of either mineral, with little ambiguity.

Physical and Chemical Properties: [3]: Both barite and celestine are fully oxidized and fully stable in the anhydrous condition (that is, they are not hygroscopic and tend not to form hydrates at low temperatures or high humidities). In this respect, they differ substantially from Mg-sulfates and from the Ca-sulfate anhydrite, $CaSO_4$, which tends to hydrate to gypsum, $CaSO_4*2H_2O$, which in turn can partly dehydrate on the surface to bassanite, $2CaSO_4*H_2O$ (plaster of Paris). In addition, they are harder than gypsum (the hardness of barite is 2.5-3.5 and of celestine is 3.0-3.5, whereas that of gypsum is 2.0), implying that they are somewhat more resistant to abrasion (for comparison, calcite has a hardness of 3.0). Their surfaces could be either be frosted or smoothed by abrasion, depending on the size of the abrading grains. They are not reported as thin coatings (unlike hematite or calcite), although they might, under the right conditions, form coatings (presumably subject to relatively rapid abrasion). Furthermore, they are substantially denser than other common nonmetallic minerals (the specific gravity of barite is 4.5, whereas that of celestine is 4.0; for comparison, that of calcite is 2.7), implying that they would be resistant to being carried off by the wind or water. In this regard, unlike calcite, they commonly occur in coarse crystals (barite) or coarse nodules (celestite) that are resistant to aqueous or other weathering. In other words, they should form lag deposits on the surface of Mars, much as they commonly do on Earth. Finally, we note they have no polymorphs, unlike calcite, which has two (aragonite and vaterite), or hematite, which has one (maghemite, which is strongly magnetic, like magnetite). Overall, their detection, as well as its implications, should be unambiguous. The only difficulty is that low temperature coatings of witherite ($BaCO_3$) or strontianite ($SrCO_3$), on top of barite or celestine, respectively, might make them difficult to detect. Such coatings are not seen in terrestrial exposures, however, and their occurrence on Mars would be entirely conjectural.

IR Detection of Sulfates: We measured airborne ("SEBASS") and ground-based ("Tonka") thermal infrared spectra of regions with barite and celestine. SEBASS (~7.5–12.5 µm, 128 bands) is the only airborne instrument available that measures spectrometer data similar to TES. Tonka (~7.5–12.5 µm, 512 bands) is the only field instrument that raster-scans thermal infrared, hyperspectral images like MiniTES.

Hyperspectral data can discriminate between the sulfate minerals present. For example, Fig. 1 shows spectra measured of Bristol Lake gypcrete and celestine samples. The offset in the band centers is also observed in SEBASS and Tonka data, and is used to map the minerals present.

Occurrences [4]**:** Barite and celestine occurrences on Earth have been much studied because of their economic uses. The main use of barite is to increase the specific gravity of drilling muds used in petroleum exploration; a secondary use of Ba (of some interest for Mars) is in radiation shielding in glass. Ba also is used in a wide variety of chemicals, ceramics, and solid state devices. Strontium is likewise used in glass for radiation shielding (TV picture tubes), and for chemicals, ceramics, and solid state devices (as well as for the red color in fireworks). Geochemically, Ba and Sr are highly soluble in aqeuous environments as chlorides, but are highly insoluble as sulfates (Ba more than Sr). Precipitation of either barite or celestine therefore generally involves mixing of a Ba or Sr-rich aqueous fluid, which has leached Ba or Sr from an igneous or other source rock at depth, with a sulfate-rich near-surface brine. Less commonly, it can also happen by replacement of evaporites rich in sulfate minerals by fluids unusually rich in Ba or Sr (typically Sr, because the Ba is preferentially removed early on). On Earth, barite and strontianite precipitation by fluid mixing and replacement occurs in a huge variety of marine and terrestrial settings, some involving environments that are probably unlikely on Mars (e.g., replacement of massive bedded limestones of biologic origin by continental brines, and oceanic precipitation above submarine hot springs). Two environments of possible interest for Mars, that we have been studying in southern California deserts, are 1) precipitation of coarsely crystalline barite in veins and faults in volcanic-hydrothermal environments and 2) precipitation of celestine as coarse nodules in modern and ancient evaporitic lake beds. The first environment has obvious application to the "hot spring" environment that has been suggested for the landing site of Mars Exploration Rover "Opportunity"; the second has obvious application to the Gusev Crater landing site of Mars Exploration Rover "Sprit".

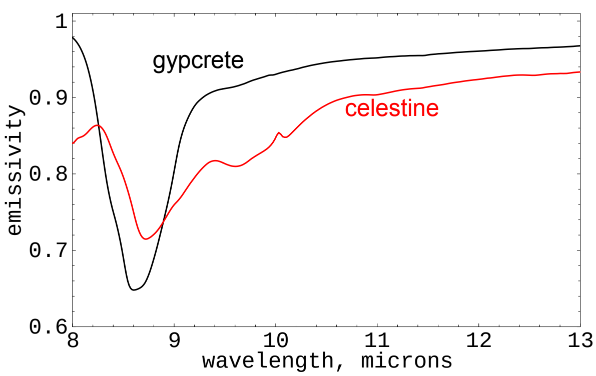

Fig. 1: Identification of sulfates using thermal infrared spectra. Offsets in the sulfate band center identify the mineral present. These are laboratory biconical reflectance spectra, measured by Paul Adams, The Aerospace Corporation.

California Occurrences [5]:

Barite: We imaged coarsely-crystalline white barite that occurs in a series of parallel hydrothermal veins cutting fractured volcanic rocks, at the southeast end of the Cady Mountains, about 5 km north of Ludlow, CA. This occurrence is known as the Hansen deposit; it was mined briefly about 1930. Hematite (fine-grained and red) is present along with barite; no sulfides were seen. Limited visible wall-rock alteration involves minor blue-green chlorite and yellow-green epidote, plus occasional pink adularia, suggesting a relatively low temperature hydrothermal (epithermal or hot springs) origin. The veins, which dip about 45 degrees northwest, range from ~1 to 4 m wide, and averaged ~2 m wide where they were mined underground [Wright et al, 1953, p. 133]. They visibly extend in surface outcrop for at least a hundred meters northwest of where they were mined. Current surface exposures are good, owing to the hard volcanic host rock.

Celestine: We imaged coarse white (up to 5 cm where visited) nodules of celestine in modern evaporitic lake sediments along the south shore of Bristol Dry Lake, slightly below outcrops of massive ground-coating "gypcrete" (pavement-like gypsum). These were briefly mined by scraping in 1942 [5, p. 191]. Bristol Lake itself is mined for a brine rich in calcium chloride, which is a hygroscopic salt that might also be common in brines on Mars [6]. We also imaged white celestine in Tertiary (possibly Miocene) steeply-dipping tuffaceous lake beds along the southern front of the Cady Mountains, near the peak Sleeping Beauty. This area is mainly called the Argos mine, after the old townsite about 5 km to the southeast. This is reported to be by far the largest strontium deposit in California, and is discontinuosly exposed along a strike length of nearly 4 km, with beds dipping 20 to 50 degrees to the south [5, p. 241-242]. Celestine beds are reported to be up to nearly 2 m thick, but with most <0.3 m thick. The stratigraphic zone containing fine-grained celestine beds is reported to be at least 80 m thick. The mines were mainly active during World Wars I and II. Current exposures are only fair, owing to the soft host rocks (lake beds). That is, surface open cuts are largely still accessible, but many underground workings appear to have collapsed.

Conclusion: Barite or celestine detection on Mars might provide a less ambiguous indicator of the presence of former abundant water than the detection of either calcite or coarsely-crystalline hematite. Barite and celestine have distinctive thermal infrared spectra, and both minerals have been detected and mapped in SEBASS images of California occurrences analogous to those that might occur on Mars. Barite would probably be most likely to occur in hydrothermal veins or hot spring environments, in association with volcanism or cratering activity, whereas celestine would be more likely to in former lake beds, possibly associated with other evaporite minerals. These two distinctive environments have been suggested for the two Mars Exploration Rover landing sites.

References. [1] Kirkland L.E. et al. (2003), Infrared stealthy surfaces: Why TES and THEMIS may miss substantial mineral deposits on Mars, *JGR*, 10.1029/2003JE002105, 108(E12), preprint www.lpi.usra.edu/science/kirkland. [2] Kirkland, L.E. et al. (2003) Hematite coatings match TES spectra of Sinus Meridiani, Mars, *LPSC XXXIV*, abs. 1944. [3] Gaines, R.V., et al., Dana's New Mineralogy, Wiley, 1997. [4] Hanor, J.S., Rev. Mineral. Geochem., 40, 193-275, 2000]. [5] Wright, L.A. et al., Calif. Jour. Mines and Geol., 49, 49-192, 1953. [6]Burt, D.M. and Knauth, L.P. (1993) JGR 108, doi:10.1029/2002JE001862.