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Evaluation of near-infrared spectra for detecting
ammonium minerals at Shoshone Geyser Basin,
Yellowstone National Park, Wyoming

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Introduction

Samples were collected from the Shoshone Geyser Basin in Yellowstone National Park (Fig. 1) to test for the presence of ammonium minerals. Eight samples were collected during a reconnaissance hike to the roadless area in early November, 1992 by Rick Hutchinson of the National Park Service. Shoshone Geyser Basin is the largest undeveloped geyser basin in the world. The presence of ammonium minerals at the geyser basin would allow for a better understanding of how the cation fits into a large active hot spring/geyser area. The presence of mercury and measurements of ammonium in water samples from Yellowstone (Hamilton and others, 1990; White and others, 1963) also suggests that hydrothermal areas within the Park may provide a favorable setting for ammonium minerals. This report is submitted as an investigator's annual report as part of the requirements for obtaining a collection permit at Yellowstone National Park.

Background

Ammonium minerals are known to occur in shallow epithermal hot spring deposits (Erd and others, 1964). One of the largest deposits of ammonium minerals occurs at Sulphur Bank, California, a modern hot springs that is actively precipitating mercury (White and Roberson, 1962). The ammonium feldspar, buddingtonite, occurs as an alteration product of hydrothermally altered rhyolite along the edge of the Sulfur Bank deposit. More recent work has shown that buddingtonite and other ammonium minerals have diagnostic spectral features in the near-infrared region near 2100 nanometers (Krohn and Altaner, 1987). Such minerals can be identified spectrally in the laboratory or by using a hand-held or other remote detectors.

Diagnostic near-infrared reflectance spectra are shown for several common mineral-types at a hot-spring (Fig 2). Clay minerals are associated with argillic hydrothermal alteration. The clay minerals kaolinite, montmorillonite, and illite have diagnostic spectral features near 2200 nanometers (Fig 2). These spectral features are related to combination tones and overtones of fundamental vibrational features associated with Al-OH in the mid-infrared wavelengths. Other minerals with spectral features possibly observed in hydrothermally-altered areas are also shown in Figure 2. Alunite is a common hydrothermal alteration product with spectral bands near 1760 and 2170 nanometers due to Al-OH and S-OH. Buddingtonite, the ammonium feldspar, has 2 absorptions bands near 2000 and 2100 nanometers that can be distinguished from the clay mineral bands. The ammonium bands are superimposed upon other spectral features that may be present in other mineral forms. The diatomite spectrum is shown to

represent amorphous silica observed in hydrothermal areas. The spectrum exhibits a shallow absorption band near 2250 nanometers resulting from Si-OH vibrational modes. The prominent spectral bands at 1400 and 1900 are related to O-H and H-O-H molecular features and are commonly indicative of loosely bound-water in the mineral. When measuring spectra in the field, these bands are obscured by water in the atmosphere.

Procedures

Near-infrared reflectance spectra of the Shoshone Geyser Basin samples were measured on a Beckman¹ Model 5240 UV spectrophotometer. Samples were labelled in an arbitrary order. The clay mineral sample was first run moist and then dried, sieved to a particle size between 75 μm and 250 μm , and rerun. The clay sample was x-rayed in a random mount to maximize reflections in order to confirm its identification. Other sample spectra were measured on the natural surfaces of rock fragments. Spectra are plotted as reflectance with respect to a Halon¹ standard.

Results

Spectrum D-673 (a, Fig. 3) of the amorphous siliceous sinter from the Shoshone Geyser basin is a key spectrum for interpreting this suite of mineral spectra. The two water bands are prominent, but in addition the shallow absorption feature for the Si-OH feature is present near 2250 nanometers. The 2250 feature, although not a symmetrical spectral band, is similar to the spectral feature observed in the diatomite spectrum and provides evidence for amorphous silica being the mineralogical component observed in the near-infrared spectra. Aines and Rossman (1984) attribute the 2250 feature to bending plus stretching motions of the Si-OH groups and show the feature present in samples of opal. Podwysocki (and others, 1985) suggest that these spectral features represent gel defects or noncrystalline silica. Because sample D-673 is relatively homogeneous, its spectrum can be compared to other spectra that might contain mineral mixtures. Amorphous silica sinter is a fairly common rock type in the Shoshone Geyser Basin.

Two samples of hydrothermally altered glacial material were thought to have some of the best chances for observing ammonium materials because the samples are composites of several different rock types. Spectra of the cemented kame sediments and the cemented kame vein filling (Spectra D-675 and D-671; b and c, Fig. 3) show the effects of Si-OH. Because of the variegated nature of the sample, clay minerals might be expected. However,

¹Brand names are given for descriptive purposes only and do not represent an endorsement by the U.S. Geological Survey.

silica cement has spectral features which dominate the other possible spectral components in the whole rock spectrum.

The spectra of sinter from the active Minute Man Geyser area show the same type of spectral features, but the band depths are greatly reduced (D-674 and D-672; a and b, Fig. 4). The temperature of the water from sample D-674 was greater than 80°C. The samples are much more friable and porous than the former cemented samples. The shallower band depths may be indicative of less bound water in the mineralogy of the fresh sinter as compared to the cemented silica samples.

The spectrum of a siliceous sinter deposit from the continuous spouter east of Shoshone Creek (D-677; c, Fig. 4) shows a large H-O-H band near 1900 nanometers, but smaller spectral bands for the O-H and Si-OH features near 1400 and 2250 nanometers respectively. The sample has a 4 mm thick black crust of presumably FeS, but the unexposed white surface was measured for better spectral contrast. The crust suggests that the sample may have been exposed at the surface. The intermediate band depths may represent an intermediate stage between the active sinters and the amorphous silica samples.

A sample of thermal clay, D-676, was collected in a plastic bag and was still moist upon its arrival at the laboratory. The O-H and H-O-H bands in the spectrum at 1400 and 1900 nanometers (D-676; b, Fig. 5) are predominant. These broad liquid water features would limit any attempt to identify the sample in a real world setting. The sample was air dried and rerun. The spectrum of the dried clay (D-676; a, Fig. 5) clearly indicates kaolinite, which was confirmed by X-ray diffraction. Clay minerals are normally good hosts for ammonium cations. The one exception is kaolinite, which does not have any suitable cation sites for NH₄ substitution.

The parent rhyolite outcrop may also be a host for ammonium, although generally concentrations in the igneous rocks are low. The sample has a dark black surface coating, probably of FeS. The spectrum (D-678; c, Fig. 5) shows a broad Fe feature, but little O-H spectral features. The coating would obscure detection of any low concentrations of ammonium in the rock.

Discussion

The origin of the nitrogen is an unresolved question for ammonium minerals found in hydrothermal systems. Nitrogen isotopic evidence is to date inconclusive (Krohn and others, in press). Many hydrothermal localities in the western U.S. are near organic-rich sedimentary or meta-sedimentary rocks, which could be sources of nitrogen. Still, the low concentrations of N in some igneous rocks suggests there may also be a magmatic component. Unlike other hot spring systems in igneous rocks, Yellowstone does have measurable amounts of ammonia in some water samples. Locomotive Springs near the Norris Geyser Basin (Fig. 1) measures 30 ppm NH₄ (White and others, 1963). The presence of

ammonium minerals from Shoshone Geyser area, inside the caldera, would have been good evidence for nitrogen in ammonium minerals originating from a magmatic source.

Ammonium minerals in hydrothermal settings are closely associated with faults and fractures where they have been mapped by in-situ or airborne methods in the western U.S. Future sampling for ammonium minerals at Yellowstone should take this observation into account. The Norris-Mammoth Corridor at the north end of the park (Fig. 1) is a likely location. The area is heavily faulted, known ammonium in waters occurs at the south end of zone, and trace concentrations of mercury are observed along these faults (Hamilton and others, 1990). The combination of these three factors are favorable for ammonium. Because it is outside the caldera, assigning an origin of the nitrogen from this area becomes more ambivalent.

Future sampling for ammonium needs to be done with some care at Yellowstone. The presence of water vapor from the hot springs and geysers makes remote or in-situ measurements difficult. Careful field sampling at drier times of the year combined with laboratory measurements appears to be a good sampling strategy. Also the ubiquitous nature of amorphous silica observed at Shoshone Geyser basin needs to be taken into account. A key consideration for finding ammonium minerals at Yellowstone is finding a host rock with a potential cation for substitution. Argillic host rocks other than kaolinite need to be sampled. Adularia described from the Norris Geyser Basin (White and others, 1988) appears to be a suitable host rock if present at the surface. The sampling of a proper host rock, location with faults and fractures, presence of trace amounts of mercury, all seem to favor the Norris-Mammoth corridor as the next place to look for ammonium minerals at Yellowstone National Park.

Summary

Ammonium minerals were not detected during a reconnaissance sampling of the Shoshone Geyser Basin at Yellowstone National Park. Several different forms of amorphous silica were observed as Si-OH spectral features in near-infrared spectra of materials from the active geyser area. Spectral features were masked by water absorption features in the argillically altered rock in its moist field state; however, the dried sample clearly showed spectral features of kaolinite. Future sampling for ammonium minerals should concentrate on first, finding a proper host lithology for cation substitution, and second, looking for areas near faults or fractures that show some trace concentrations of mercury.

List of Figures

Figure 1 - Location map for Shoshone Geyser Basin (arrow) in southwestern Yellowstone National Park, Wyoming. Map shows relation of present and fossil hydrothermal areas to caldera structure (Modified from White and others, 1988).

Figure 2 - Comparison of near-infrared diffuse reflectance spectra for selected minerals commonly observed near hydrothermally-altered areas. Spectra are displaced vertically for viewing purposes. Tics on ordinate are 10% reflectance, except for buddingtonite, which are 5% reflectance.

Figure 3 - Visible and near-infrared relative reflectance spectra from samples near Shoshone Geyser Basin showing spectral features related to silica and hydroxyl (Si-OH). D-673 (3a) is amorphous siliceous sinter; D-675 (3b) is a cemented kame sediment; and D-671 (3c) is a cemented kame vein filling. Reflectance is measured with respect to a Halon¹ standard. Tics on ordinate are at intervals of 10% reflectance. Numbers at right are reflectance values at 2500 nanometers.

Figure 4 - Visible and near-infrared relative reflectance spectra of sinter samples near Shoshone Geyser Basin. D-674 (4a) is a siliceous sinter from a continuous spouter, northeast of Minute Man geyser; D-672 (4b) is an arenaceous sinter from an active spring northeast of Minute Man geyser; and D-677 (4c) is a siliceous sinter with FeS crust from a continuous spouter east of Shoshone Creek. Graph coordinates are the same as Figure 3.

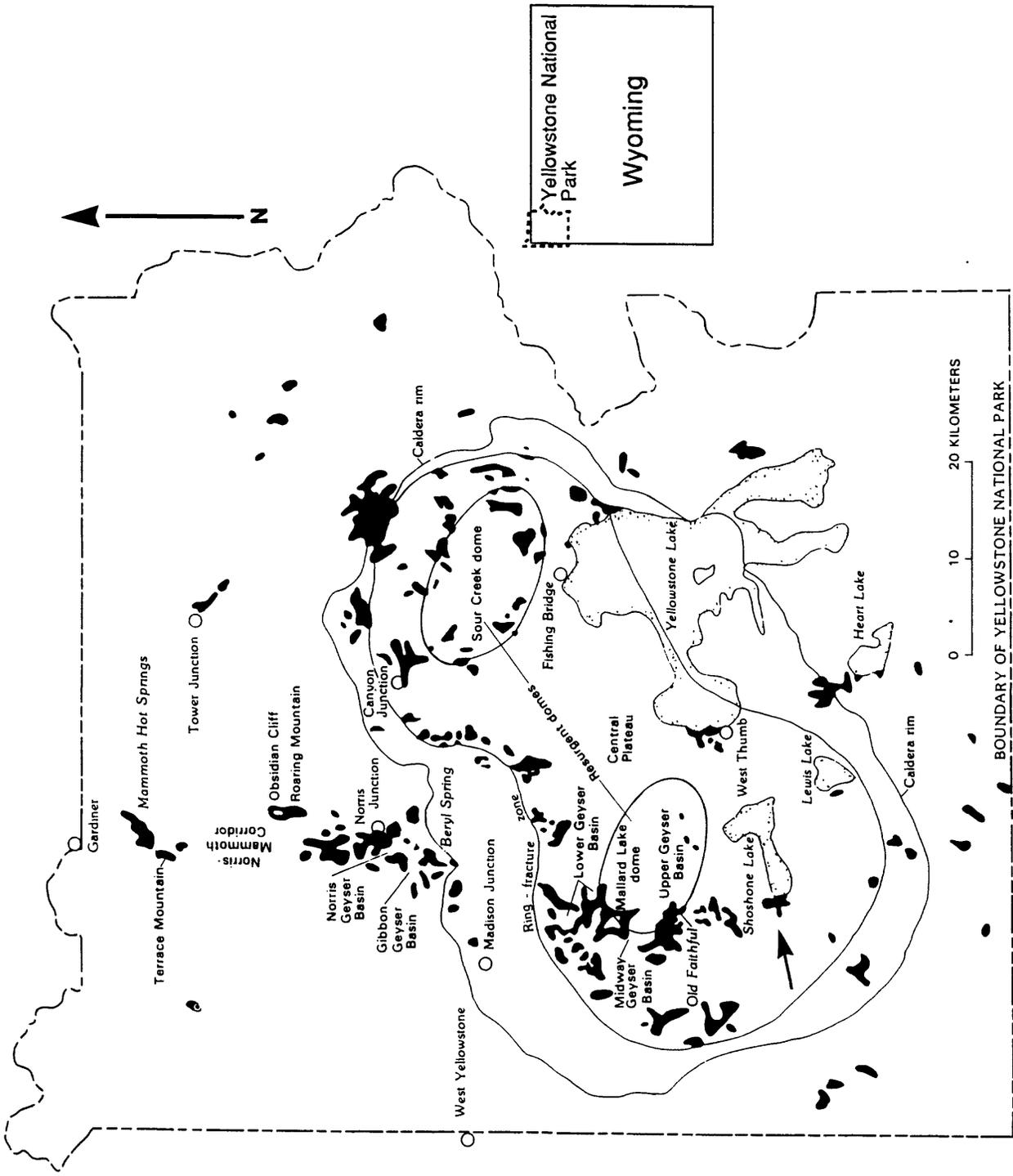
Figure 5 - Visible and near-infrared reflectance spectra of rock samples from the rhyolite outcrop area near Shoshone Geyser Basin. D-676 is an altered thermal clay near the rhyolite outcrop, southwest of Shoshone Geyser Basin. Clay sample was collected and measured moist (5b) and then rerun dried (5a). D-678 (5c) is the rhyolite outcrop at the southwest margin of the Shoshone Geyser Basin. Graph coordinates are the same as Figure 3.

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Explanation

-  Hydrothermal Area
-  Lake
-  Town



Yellowstone National Park
Wyoming

0 10 20 KILOMETERS

BOUNDARY OF YELLOWSTONE NATIONAL PARK

Figure 1

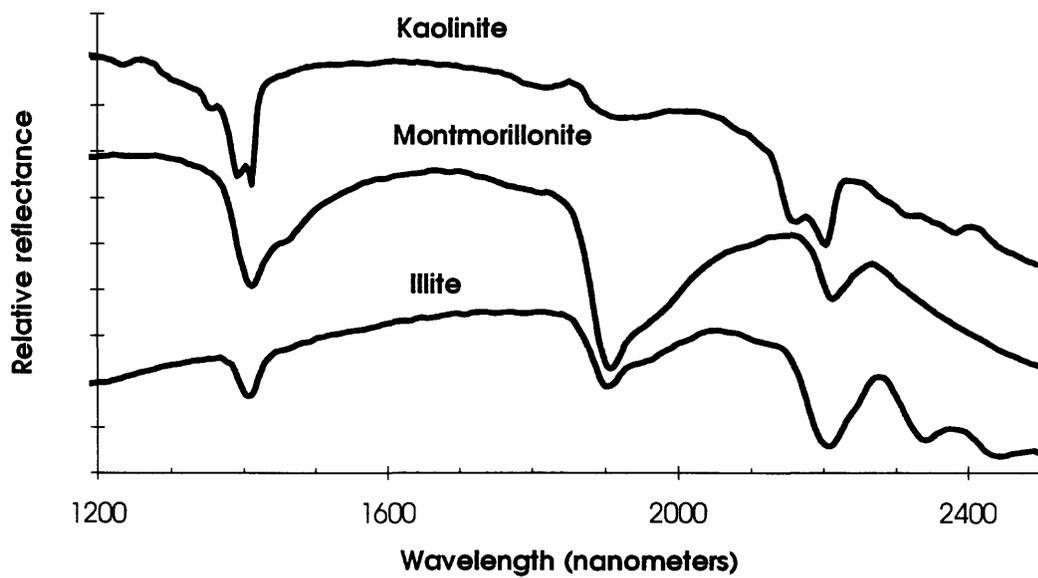
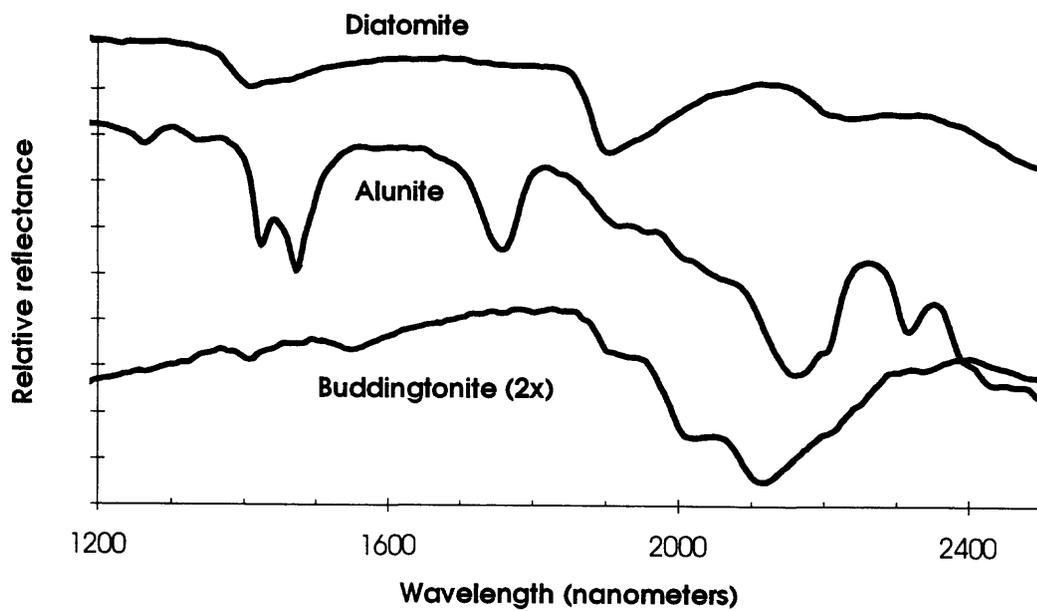


Figure 2

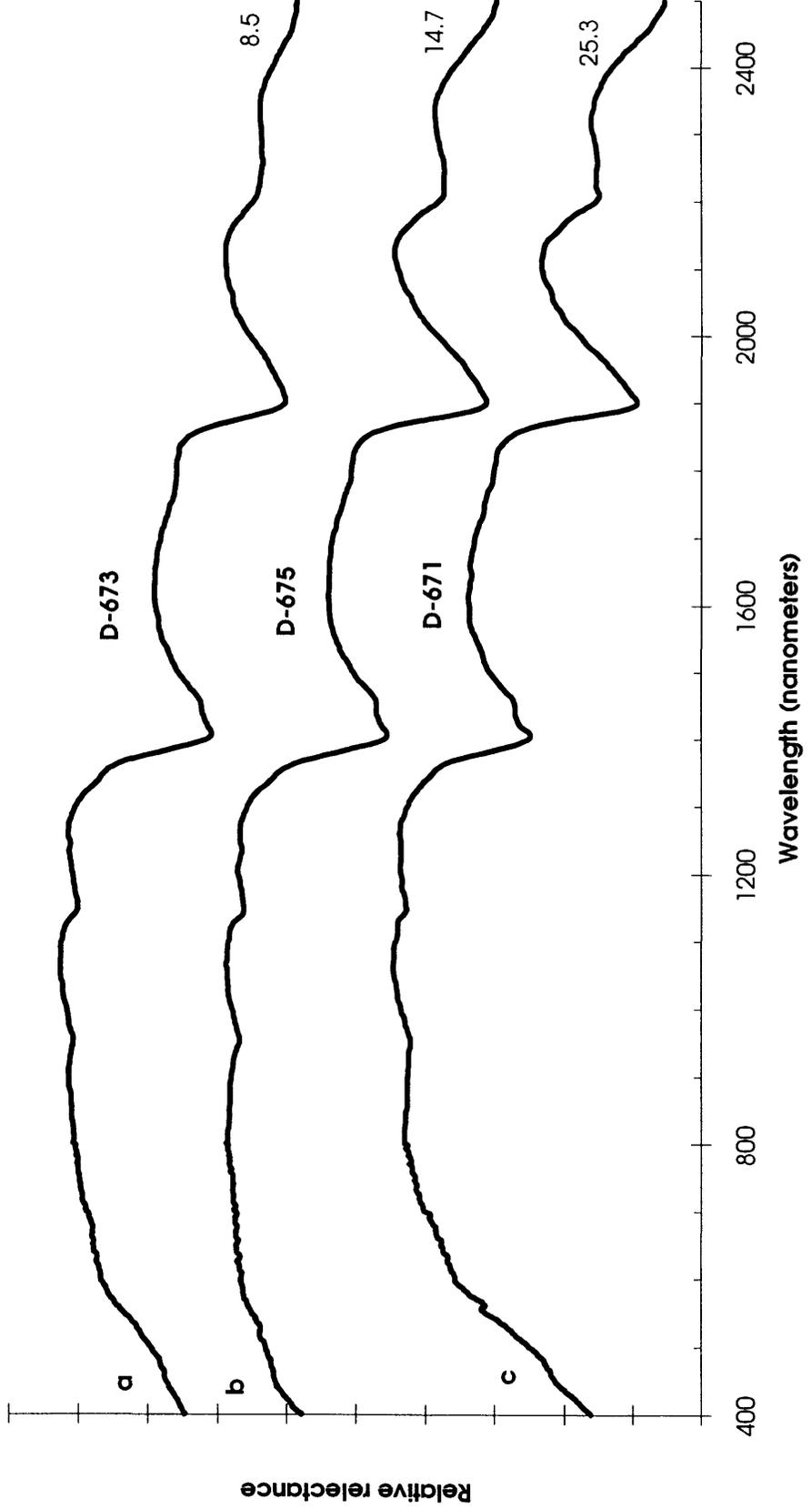


Figure 3

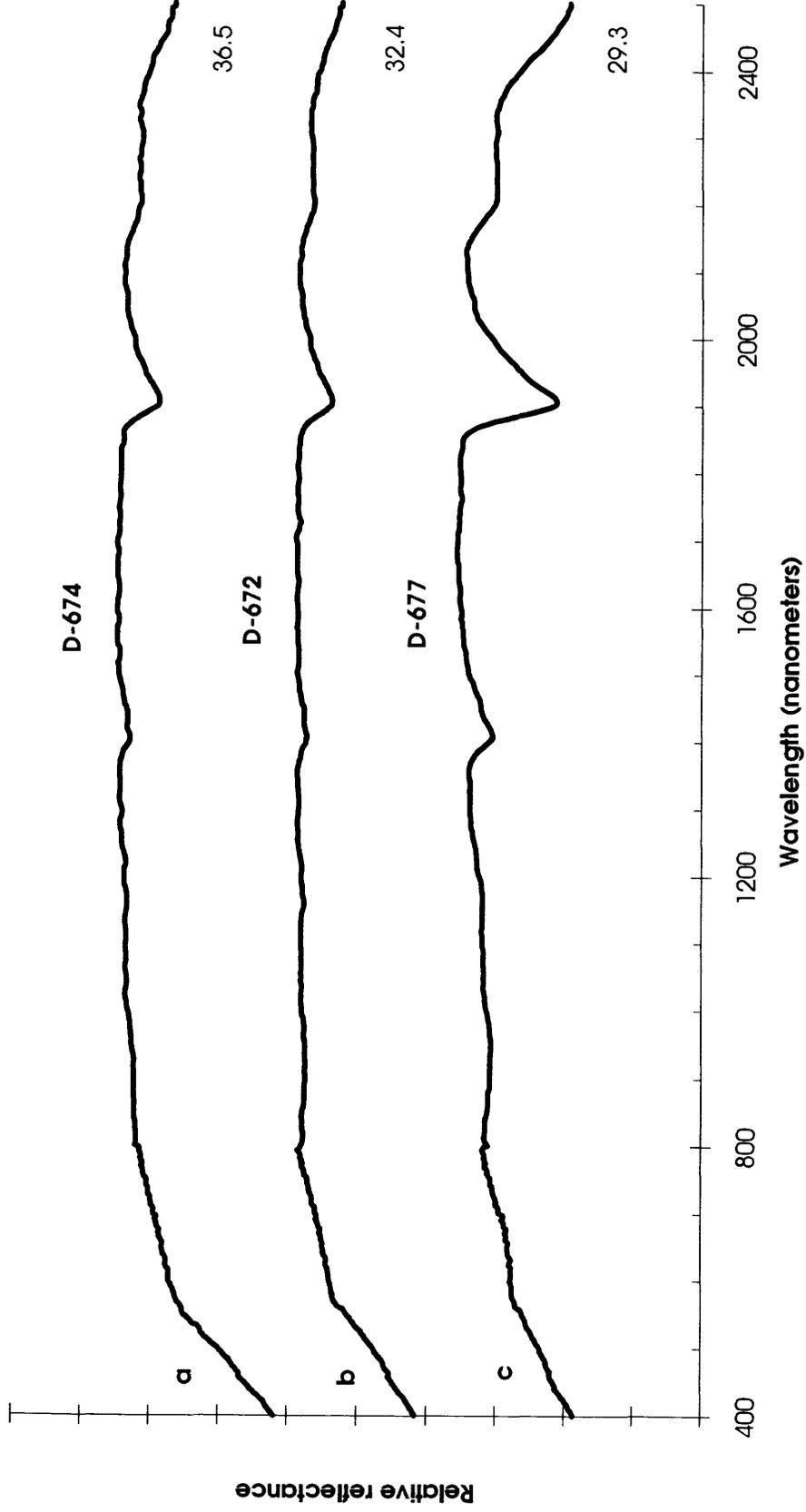


Figure 4

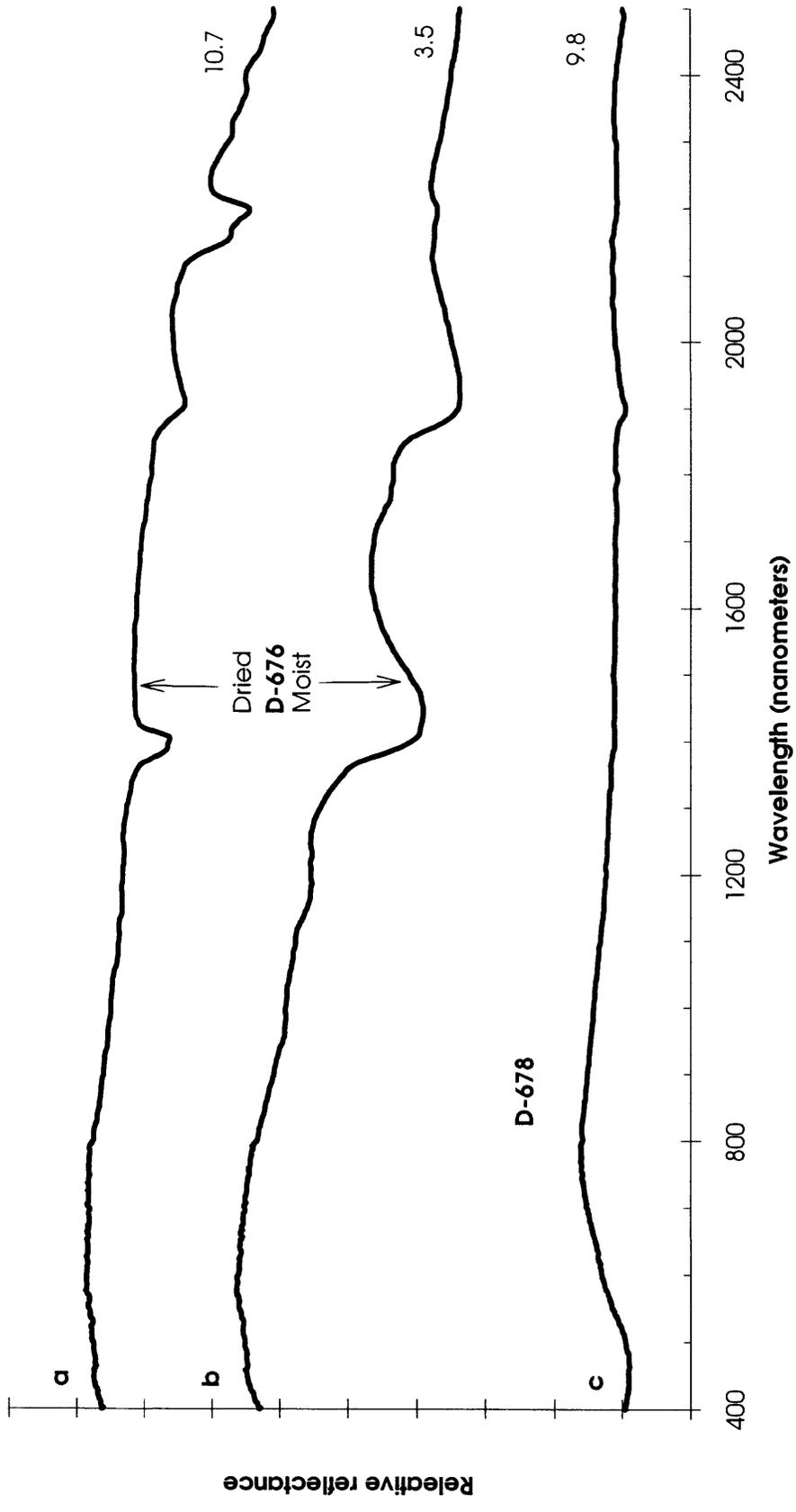


Figure 5