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12. DATA REPORT: VISIBLE AND NEAR-INFRARED SPECTROSCOPY AS AN INDICATOR OF HYDRATION IN THE UPPER OCEANIC CRUST OF ODP SITE 1256[1]

Marcie J. Kerneklian[2,3] and Richard D. Jarrard[2]

ABSTRACT

For extrusive basalts of the upper oceanic crust, near-infrared radiation is reflected with a spectrum that is sensitive to the extent of crustal alteration. A published pilot study of basalts from Hole 801C showed that reflectance-based apparent alteration correlated with independent geophysical indicators of alteration (e.g., matrix density). This study shows that reflectance-based hydration correlates with geochemical measurements of structural water percentage and that air-dried archive-half cores exhibit more reflectance-based hydration than do vacuum-dried minicores. We calibrate the spectral response of visible and near-infrared spectroscopy (VNIS) with 907 measurements from seven basalt sites. The relationship between VNIS hydration estimates and geochemical measurements of structural water was determined, and a VNIS-based estimate of relative smectite abundance was produced by factor analysis of three spectral characteristics. We used this calibration to estimate variations in hydration and smectite abundance throughout the 502-m section of upper oceanic crust at Ocean Drilling Program Site 1256, based on 2327 VNIS measurements on archive-half cores and 88 measurements on minicores.

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[2] Department of Geology and Geophysics, University of Utah, Salt Lake City UT 84112, USA. Correspondence author: **jarrard@earth.utah.edu**

[3] Present address: Newmont Mining Corporation, Golconda NV 89414, USA.

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INTRODUCTION

Ocean Drilling Program (ODP) Site 1256, which obtained a 502-m section of oceanic crust formed at a superfast spreading rate, encountered a low degree of crustal alteration compared to other in situ penetrations (Shipboard Scientific Party, 2003). This study analyzes basalts from Site 1256 using visible and near-infrared spectroscopy (VNIS) as an indicator of crustal alteration. VNIS is a mineral identification technique that measures the absorption spectrum, in visible and near-infrared bands (350–2500 nm), of a light beam reflected from any surface.

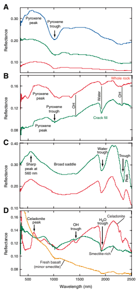
VNIS has several advantages over traditional Deep Sea Drilling Project (DSDP) and ODP analytical techniques for analyzing basalt alteration:

1. It is extremely fast, at 10 s per measurement plus any sample handling and record keeping.
2. It is nondestructive, as there is no need to deplete the DSDP/ODP basalt library by taking samples; one can make a measurement without even removing a sample from its core liner.
3. The noninvasiveness of VNIS makes it appropriate for both archive-half cores and working-half cores, allowing analysis of previously depleted basalt intervals.
4. VNIS is particularly sensitive to hydration and smectite concentration, both of which have presented challenges to interlaboratory measurement consistency.

METHODS: VNIS MEASUREMENT

Absorption spectroscopy measures the spectrum of light reflected from rock surfaces. Light is absorbed by minerals at and near the surface of the rock because of both electronic and vibrational processes (Clark et al., 1990; Hapke, 1993; Clark, 1995). Normal modes of characteristic vibrations of OH^- bonds are particularly useful for mineral identification. Water, Mg-OH, Al-OH, and Fe-OH absorption bands are identifiable in the near-infrared. Types of identifiable minerals depend on the frequency band of the instrument. For example, the split-core analysis track (Mix et al., 1995) detects electronic processes at visible wavelengths (250–900 nm). We use the FieldSpec Pro FR portable spectroradiometer because its wide bandwidth (350–2500 nm) enables identification of hydrous minerals.

Figure F1 illustrates some VNIS responses in basalts. The volumetrically dominant minerals in most basalts are pyroxene and plagioclase. As plagioclase is spectrally featureless, it is undetectable by VNIS. The dominant spectral signature in the fresh basalts of Figure F1 is from pyroxene, with a peak at 500–900 nm and an absorption trough at 1000 nm. Smectites, with an OH^- absorption band at 1418 nm and a strong water absorption band at 1900–1930 nm, can be detected at modal abundance of only a few percent (Vanden Berg and Jarrard, 2006). A second major alteration mineral, celadonite, is spectrally distinct from smectite and pyroxene (Fig. F1). When abundant, iron oxyhydroxides (Fe[O,OH]x) may also be identifiable with VNIS because of their OH^- absorption bands, but that is beyond the scope of this study because we lacked local iron oxyhydroxide standards. Other alteration minerals,


F1. VNIS spectra from basalts, p. 9.

such as calcium carbonate and zeolites, have distinctive spectral signatures but are seldom abundant enough for detection by VNIS.

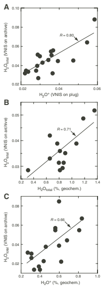
Previous VNIS Analyses of Basalts

Jarrard et al. (2003) used VNIS to estimate alteration of physical property samples from ODP Hole 801C. Pore water has the same 1418-nm OH^- and 1910-nm water absorption bands as hydration minerals, so they vacuum dried samples prior to VNIS measurement. Trough depths of 1418-nm OH^- absorption and 1910-nm water absorption, each normalized to adjacent wavelengths outside the absorption band, were highly correlated ($R = 0.882$), so they combined them into a single measure of hydration intensity among the Hole 801C basalts. Jarrard et al. (2003) found that VNIS-based hydration significantly correlated with porosity, matrix density, and permeability. They concluded from these and other patterns that higher porosity is responsible for higher permeability and therefore higher fluid flow rates, which fosters alteration, particularly the hydration reactions that generate clays.

Nondestructive VNIS measurements can be undertaken on archive-half cores rather than on dried core plugs, thereby determining total structural water ($H_2O^- + H_2O^+$) rather than just H_2O^+. The core surface must be dry enough to avoid mistaking pore water for structural water. The core interior need not be dry, just the few tens of microns adjacent to the surface and accessible to reflected light. DSDP and ODP basalts do dry substantially during the several hours between core splitting and placement in D-tubes. When first removed from the refrigerator, basalt core surfaces quickly develop condensation; therefore, we delayed VNIS measurements until the surface had visibly dried.

We undertook two feasibility studies of determining basalt hydration by direct VNIS measurement on archive-half cores. First, we compared VNIS spectra for 18 vacuum-dried basalt core plugs from Sites 319 and 470 to those measured on corresponding portions of the archive half. Depth of the 1910-nm water trough for archive-half data is uncorrelated with porosity but is correlated to core plug VNIS results, with higher values for archive data because of H_2O^- in the latter (Fig. F2A). Considerable dispersion is evident; both measurements were from the same basalt piece but not the same portion of each piece, and alteration heterogeneity within pieces is substantial. A second feasibility study (Fig. F2B, F2C) compared VNIS-based hydration measurements on Site 428 archive-half cores to published analyses of total water (Srivastava et al., 1980) and H_2O^+ (Humphris et al., 1980). Despite the small alteration range (fresh to slightly altered) within this site, significant hydration variations were detectable, suggesting that the much wider range of observed alteration intensities elsewhere should be easily resolvable.

F2. Archive-half core hydration vs. dried plug hydration, total water, and H_2O^+, p. 10.



Measurement Technique

Light reflectance at a bandwidth of 350–2500 nm was measured for each sample using the Analytical Spectral Devices (ASD) FieldSpec Pro FR portable spectroradiometer. The light source was a high-intensity light probe fitted with a quartz halogen bulb and equipped with a built-in direct current stabilizer. The fiber-optic detector cable, which conveys the reflected light to the spectrometer, is inserted within the light probe. A split-core measurement is taken by placing the light probe directly onto the split core, thereby illuminating and measuring a 2.6-cm-diameter area of core. A plug sample measurement is taken by inserting the sample a few millimeters within the 2.6-cm-diameter aperture of the light probe. The reflected light is sent via the fiber-optic cable to the spectrometer, where the spectral data are collected and saved on a minicomputer. Before beginning a batch of measurements, spectral response of the light source needs to be normalized to a 100% reflectance level by calibrating the light source to a Spectralon white $BaSO_4$ calibration plate. This calibration is repeated between each core section every five sample measurements or as needed due to instrument drift.

The ASD spectroradiometer comprises three spectrometers, each of which measures a different bandwidth. Subtle sensitivity differences among these spectrometers generate small vertical offsets at each boundary between adjacent spectrometer wavelengths. The algorithm of Vanden Berg and Jarrard (2002) was applied to the raw spectral data to remove these offsets. The 350- to 450-nm portion of the spectrum is sometimes noisy due to fluctuations in the light source, but this does not interfere with identification of key features and so is ignored.

During Leg 206, 2327 VNIS measurements were made on the archive-half split cores at an average spacing of 12 cm. Our VNIS sampling generally avoided veins. Spectra were recorded after the cores had been allowed to air dry so that no moisture would be present on or near the surface. VNIS measurements on 88 minicore samples drilled from cores were measured postcruise after vacuum drying at 60–100 mTorr for several days.

Estimation of Hydration and Alteration Minerals from VNIS Spectra

Several methods have been proposed for analysis of VNIS data. Most aim to identify the spectrally dominant mineral, rather than estimate relative abundances of spectrally significant minerals (Clark et al., 2003). Our VNIS studies seek to determine semiquantitative mineral concentrations. For sediments, this is accomplished by using a suite of local ground-truth measurements (e.g., X-ray diffraction) to calibrate characteristic VNIS absorption features. Our first step in analyzing the ground-truth spectra is to identify areas of the recorded spectrum that react differently to different minerals. Analysis of overall spectrum shape is inappropriate because it is sensitive to minor mineralogic components. For VNIS-based mineralogy of equatorial Pacific sediments, Vanden Berg and Jarrard (2002, 2006) selected about a dozen spectral features that might be significant then calibrated spectral response in one of two ways: (1) multiple regression of each spectral response (S) on mineral fractions (F) to determine the coefficient matrix (K), followed by matrix inversion to generate the relationship $F = K^{-1}S$ for determining mineralogy of unknowns from observed spectral responses; or (2) direct multiple regression of mineral percentage on the suite of measured spectral features. These approaches are likely to work for rocks with 2–4 spectrally significant minerals; they may not succeed in more complex mineralogies. Furthermore, samples should be dry because the spectral signature of pore water dominates some spectral features of mineralogical origin.

For basalts, we begin by focusing on a small number of spectral features known to be associated with hydration and smectite, rather than a large number of spectral features that *may* be relevant. Our shipboard hydration estimates (Shipboard Scientific Party, 2003), based on archive-half VNIS spectra, used the algorithm developed for Site 801 (Jarrard et al., 2003), combining the 1418-nm OH^- absorption band and the 1910-nm H_2O absorption band. The postcruise analyses, in contrast, use refined estimates of both hydration and alteration mineralogy.

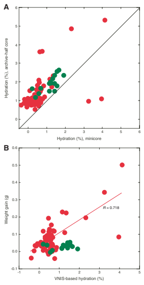
Seeking robust VNIS-based measures of basalt hydration and smectite, we obtained 907 VNIS spectra from seven DSDP basalt sites (Holes 238, 319A, 428A, 470A, 482B, 504B, and 597C) with a wide range of compositions and crustal ages. These measurements included VNIS spectra from the same depths as 145 published geochemical measurements of total water; VNIS data were from archive-half cores, whereas the geochemical data were from working-half samples.

Hydration is expected to be directly related to the 1900- to 1930-nm water absorption trough (Fig. **F1**), but this trough can be quantified in several ways. We use the ratio of reflectance at the 1910-nm trough to that of an adjacent peak at 2138 nm as a spectral measure of hydration. When this measure is compared to the published geochemical analyses of total water, linear regression permits conversion from 1910-nm trough ratio to total water: $H_2O_{total} = 15.42 - 14.22x$ (trough ratio), $R = -0.638$. The correlation between the two is only moderate, partly because of the large difference in sample volume and especially because of varied techniques for analyzing H_2O among the many included sites.

For smectite estimation from VNIS, we used three spectral features (Fig. **F1**): the 1418-nm OH^- trough, a 2315-nm OH^- trough, and slope of the overall spectrum (as given by the difference between reflectance at 500 and 1700 nm). The usefulness of the latter stems from the fact that fresh basalts are more reflective at visible wavelengths than in the near-infrared, whereas the opposite is true for smectites (e.g., compare the overall spectrum slope of smectite crack fill to that of fresh basalts in Fig. **F1**). To combine these three spectral features, we applied factor analysis to these three values for the 907 spectra from assorted basalt sites. The first factor (or principal component), accounting for 68.4% of the total variance in these three spectral features, is here interpreted as our best estimate of relative abundance of smectite. The most negative values indicate lowest smectite abundance, whereas strongly positive values indicate high smectite abundance, but we had no independent petrologic data to ground-truth a conversion from relative abundance to smectite percentage.

Smectite, which is the most common alteration mineral in basalts of the upper oceanic crust (Alt, 1995; Alt and Teagle, 2000), contains an interlayer water, so the 1910-nm water absorption band can be an additional diagnostic feature in the smectite calculation. Not surprisingly, the correlation between VNIS-based hydration and VNIS-based smectite is high ($R = 0.876$).

F3. VNIS-based hydration of air-dried archive-half cores and vacuum-dried minicore samples, p. 11.



RESULTS: VNIS-BASED HYDRATION AND SMECTITE FOR SITE 1256 BASALTS

Archive vs. Minicore

Comparison of VNIS-based hydration from minicores to results of nearby archive-half measurements for Site 1256 (Fig. **F3A**) shows the same two patterns seen previously in our pilot studies (Fig. **F2A**): (1) the two hydration measurements are correlated and (2) archive-half hydration results are systematically higher than minicore hydrations. These patterns are confirmed despite significant differences in the two experiments, such as different sites, different methods of quantifying VNIS-based hydration, hours vs. years between core splitting and archive-half measurement, and inexact depth pairing (up to 15 cm apart) for the Site 1256 measurements. The minicores were vacuum dried, a process that drives off not only the pore water but also some smectite interlayer water. The archive-half cores were allowed to air dry, removing pore water but not interlayer water. Consequently, archive measurements detect total structural water ($H_2O^- + H_2O^+$), whereas minicore measurements detect just H_2O^+.

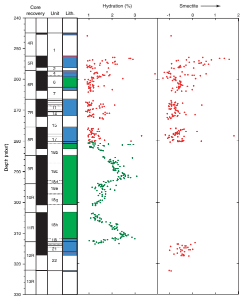
Weight Gain

Smectite interlayer water is readily lost during oven drying (e.g., Brown and Ransom, 1996) or vacuum drying. It is also partially regained by absorption of atmospheric water, depending on the humidity of the ambient air. We commonly observe that the measured weight of basalt samples gains 0–2 mg during the first 1–2 hr after vacuum drying. We confirmed that reabsorption of smectite interlayer water produces this weight gain with the following experiment. Following minicore drying and VNIS measurement of the Site 1256 samples, they were exposed to air for ~3 months and then their masses were remeasured. The magnitude of weight gain was proportional to the amount of VNIS-based alteration (Fig. **F3B**). This pattern holds for most of the Site 1256 extrusives because smectite is their primary hydration mineral (Shipboard Scientific Party, 2003). It does not hold for the ponded lava flow (green dots in Fig. **F3B**), which has undergone local high-temperature alteration and hydration (Shipboard Scientific Party, 2003).

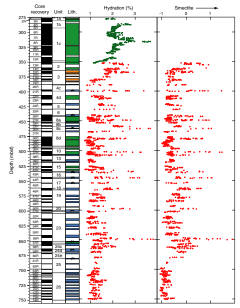
Depth-Dependent Alteration Patterns

Figures **F4** and **F5** summarize the variations in hydration and smectite with depth in Holes 1256C and 1256D based on the VNIS spectra. Hydration percentage was calculated from all spectra, but relative abundance of smectite was not calculated for ponded lava flow samples because of their more complex alteration mineral assemblage. These alteration estimates contrast with (and are only weakly correlated with) the shipboard alteration analyses resulting from logging of >6000 veins (Shipboard Scientific Party, 2003). Because our VNIS sampling generally avoided veins, we measured matrix alteration rather than crack alteration. Both are closely linked to fluid flux, but the matrix permeabilities responsible for matrix alteration and producing a correlation of VNIS-based hydration with permeability (Jarrard et al., 2003) are several orders of magnitude lower than crack permeabilities. These VNIS-based alteration estimates, like the shipboard vein studies which they complement, show that the extrusive basalts of Site 1256 exhibit pervasive, low-level but detectable, heterogeneous alteration.

F4. Hole 1256C core recovery, extrusive style, and VNIS-based hydration and smectite, p. 12.



F5. Hole 1256D core recovery, extrusive style, and VNIS-based hydration and smectite, p. 13.



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REFERENCES

Alt, J.C., 1995. Subseafloor processes in mid-ocean ridge hydrothermal systems. *In* Humphris, S.E., Zierenberg, R., Mullineaux, L., and Thomson, R. (Eds.), *Seafloor Hydrothermal Systems: Physical, Chemical, Biological and Geological Interactions within Hydrothermal Systems*. Geophys. Monogr., 91:85–114.

Alt, J.C., and Teagle, D.A.H., 2000. Hydrothermal alteration and fluid fluxes in ophiolites and oceanic crust. *In* Dilek, Y., Moores, E., Elthon, D., and Nicolas, A. (Eds.), *Ophiolites and Oceanic Crust: New Insights from Field Studies and the Ocean Drilling Program*. Spec. Pap.—Geol. Soc. Am., 349:273–282.

Brown, K.M., and Ransom, B., 1996. Porosity corrections for smectite-rich sediments: impact on studies of compaction, fluid generation, and tectonic history. *Geology,* 24(9):843–846. **doi:10.1130/0091-7613(1996)024<0843:PCFSRS>2.3.CO;2**

Clark, R.N., 1995. Reflectance spectra. *In* Ahrens, T.J. (Ed.), *Rock Physics and Phase Relations: A Handbook of Physical Constants:* Washington (Am. Geophys. Union), 178–188.

Clark, R.N., King, T.V.V., Klejwa, M., Swayze, G.A., and Vergo, N., 1990. High spectral resolution reflectance spectroscopy of minerals. *J. Geophys. Res., [Solid Earth Planets],* 95(8):12653–12680.

Clark, R.N., Swayze, G.A., Livo, K.E., Kokaly, R.F., Sutley, S.J., Dalton, J.B., McDougal, R.R., and Gent, C.A., 2003. Imaging spectroscopy: Earth and planetary remote sensing with the USGS tetracorder and expert systems. *J. Geophys. Res.,* 108(E12):5131. **doi:10.1029/2002JE001847**

Hapke, B., 1993. *Introduction to the Theory of Reflectance and Emittance Spectroscopy:* New York (Cambridge Univ. Press)

Humphris, S.E., Thompson, R.N., Gibson, I.L., and Marriner, G.F., 1980. Comparison of geochemistry of basalts from the East Pacific Rise, OCP Ridge and Siqueiros Fracture Zone, Deep Sea Drilling Project, Leg 54. *In* Rosendahl, B.R., Hekinian, R., et al., *Init. Repts. DSDP,* 54: Washington (U.S. Govt. Printing Office), 635–649.

Jarrard, R.D., Abrams, L.J., Pockalny, R., Larson, R.L., and Hirono, T., 2003. Physical properties of upper oceanic crust: Ocean Drilling Program Hole 801C and the waning of hydrothermal circulation. *J. Geophys. Res.,* 108(B4):2188. **doi:10.1029/2001JB001727**

Mix, A.C., Harris, S.E., and Janecek, T.R., 1995. Estimating lithology from nonintrusive reflectance spectra: Leg 138. *In* Pisias, N.G., Mayer, L.A., Janecek, T.R., Palmer-Julson, A., and van Andel, T.H. (Eds.), *Proc. ODP, Sci. Results,* 138: College Station, TX (Ocean Drilling Program), 413–427. **doi:10.2973/odp.proc.sr.138.121.1995**

Shipboard Scientific Party, 2003. Site 1256. *In* Wilson, D.S., Teagle, D.A.H., Acton, G.D., *Proc. ODP, Init. Repts.,* 206: College Station, TX (Ocean Drilling Program), 1–396. **doi:10.2973/odp.proc.ir.206.103.2003**

Srivastava, R.K., Emmermann, R., and Puchelt, H., 1980. Petrology and geochemistry of basalts from Deep Sea Drilling Project Leg 54. *In* Rosendahl, B.R., Hekinian, R., et al., *Init. Repts. DSDP,* 54: Washington (U.S. Govt. Printing Office), 671–693.

Vanden Berg, M.D., and Jarrard, R.D, 2002. Determination of equatorial Pacific mineralogy using light absorption spectroscopy. *In* Lyle, M.W., Wilson, P.A., Janecek, T.R., et al., *Proc. ODP, Init. Repts.,* 199: College Station, TX (Ocean Drilling Program), 1–20. **doi:10.2973/odp.proc.ir.199.105.2002**

Vanden Berg, M.D., and Jarrard, R.D., 2006. Data report: high-resolution mineralogy for ODP Leg 199 based on reflectance spectroscopy and physical properties. *In* Wilson, P.A., Lyle, M., and Firth, J.V. (Eds.), *Proc. ODP, Sci. Results,* 199: College Station, TX (Ocean Drilling Program), 1–23. **doi:10.2973/odp.proc.sr.199.203.2006**

Figure F1. VNIS spectra from basalts. **A.** Fresh basalts exhibit a pyroxene peak and trough. **B.** Crack fill is mostly smectite, with strong water and OH^- absorptions, and weak basalt pyroxene; altered whole rock has a signature intermediate between smectite and fresh-rock pyroxene. **C.** Celadonite is distinguished from smectite by peak at 560 nm and trough/peak at 2400 nm. **D.** Examples of these features at Site 1256.

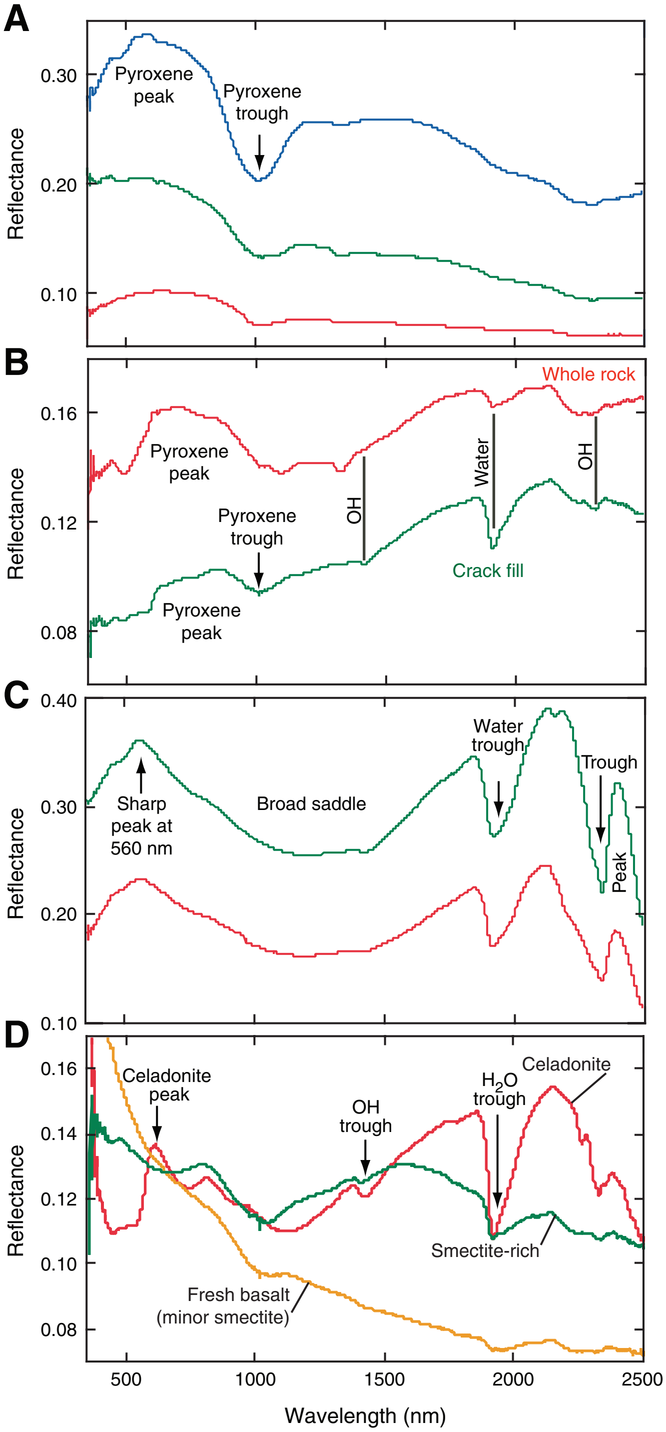

Figure F2. Pilot studies comparing visible and near-infrared spectroscopy (VNIS)-based hydration on archive-half cores (y-axis, given as trough depth, not percent) to VNIS-based hydration on (**A**) dried plugs from Sites 319 and 470 and geochemical measurements from Site 428 of (**B**) total water and (**C**) H_2O^+.

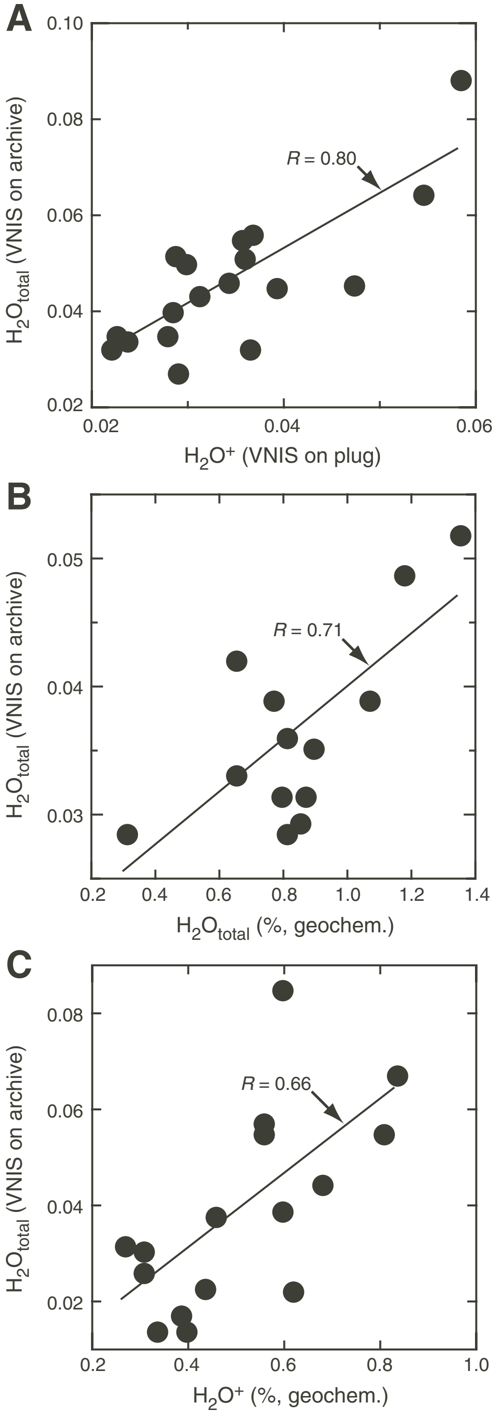

Figure F3. **A.** Visible and near-infrared spectroscopy (VNIS)-based hydration can be determined on either air-dried archive-half cores or vacuum-dried minicore samples; the correlation between the two confirms that both hydration measures see structural water, not pore water. Vacuum drying removes some structural (interlayer) water from smectites, so hydration is systematically higher in archive-half data than in minicore data. **B.** Prolonged exposure of minicores to air permits interlayers to absorb water from air; samples with abundant hydrated smectites gain more weight. Red dots = flows and pillows in which smectite is the most common alteration mineral, green dots = ponded lava flow with a more complex alteration assemblage.

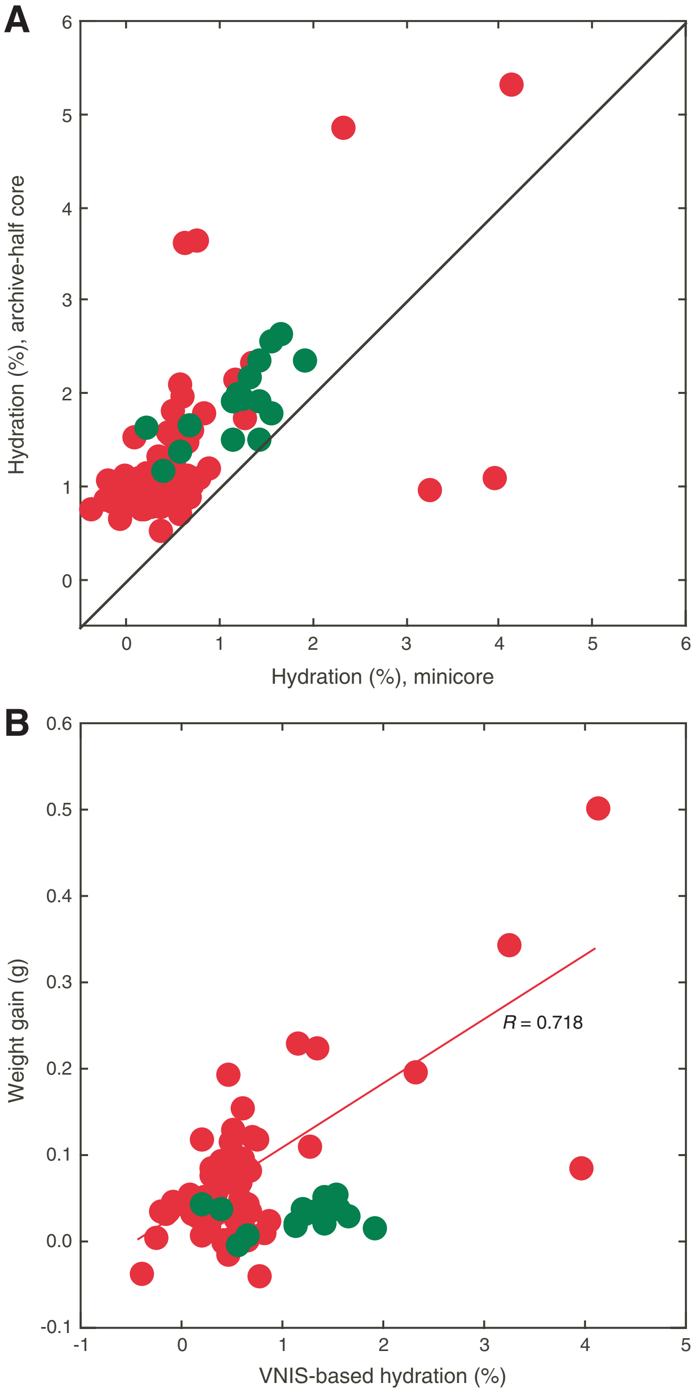

Figure F4. Hole 1256C core recovery, extrusive style, VNIS-based hydration, and VNIS-based smectite. Smectite values are based on a factor-analysis scale in which more positive values indicate higher relative abundance of smectite. Extrusive styles: sheet flows (blue) and massive flows (green). VNIS colors: ponded lava flow (green dots), other extrusives (red dots). Smectite was not estimated for data from the ponded lava flow because of complex alteration mineralogy there.

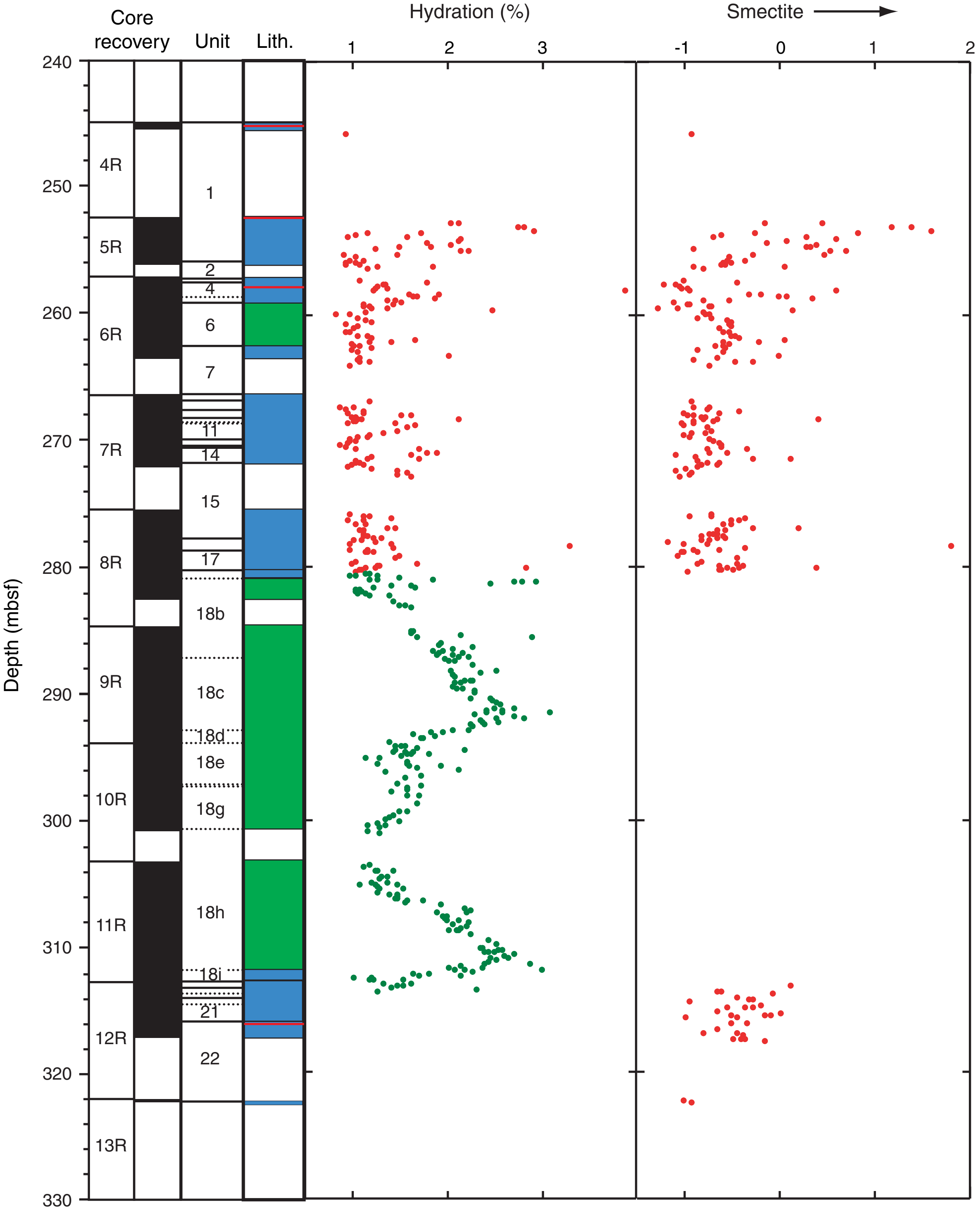

Figure F5. Hole 1256D core recovery, extrusive style, VNIS-based hydration, and VNIS-based smectite (5-point averages). Smectite values are based on a factor-analysis scale in which more positive values indicate higher relative abundance of smectite. Extrusive styles: sheet flows (blue), massive flows (green), and pillows (orange). VNIS colors: ponded lava flow (green dots), other extrusives (red dots). Smectite was not estimated for data from the ponded lava flow because of complex alteration mineralogy there.