Water in Earth's Mantle: The Role of Nominally Anhydrous Minerals

DAVID R. BELL AND GEORGE R. ROSSMAN

Most minerals of Earth's upper mantle contain small amounts of hydrogen, structurally bound as hydroxyl (OH). The OH concentration in each mineral species is variable, in some cases reflecting the geological environment of mineral formation. Of the major mantle minerals, pyroxenes are the most hydrous, typically containing ~200 to 500 parts per million H_2O by weight, and probably dominate the water budget and hydrogen geochemistry of mantle rocks that do not contain a hydrous phase. Garnets and olivines commonly contain ~1 to 50 parts per million. Nominally anhydrous minerals constitute a significant reservoir for mantle hydrogen, possibly accommodating all water in the depleted mantle and providing a possible mechanism to recycle water from Earth's surface into the deep mantle.

WATER (*1*) HAS AN IMPORTANT INFLUENCE ON THE BEhavior of molten rock systems. The variability in style and vigor of volcanic eruptions is just one manifestation of this effect. Small amounts of water or hydroxyl (OH) may also enter the structure of many minerals, the chemical formulas of which indicate that they are anhydrous. These hydrous components can have a disproportionately large influence on the physical and chemical properties of silicate minerals. They may modify the mechanical strength of the host phase, increase its internal rate of ionic diffusion (*2*), modify its dielectric properties (*3*), influence its rate of weathering (*4*), change its response to radiation damage (*5*), influence its optical properties, and modify its stoichiometry.

Interest in the hydrous components in nominally anhydrous minerals was stimulated by early studies of the influence of water on the mechanical strength of quartz (*6*), one of the commonest nominally water-free minerals of Earth's crust. Spectroscopic studies showed that quartz can contain both water molecules and OH groups and that the OH groups were crystallographically oriented, as evidenced by their anisotropic absorption of infrared (IR) radiation (*7*). Subsequently, IR spectroscopic studies of a variety of minerals demonstrated that a trace amount of OH is a common constituent of most rock-forming minerals of Earth's crust and upper mantle (*8, 9*) (Table 1).

Although the concentrations of OH (typically tens to hundreds parts per million H_2O by mass) in nominally anhydrous minerals are often too low to allow the acquisition of precise structural information, the OH is easily detected by IR spectroscopy and can be quantified (*10*). Systematic studies of the variability of OH content of nominally anhydrous minerals of natural origin have consistently revealed that for any given mineral species those samples of high-pressure or mantle origin are commonly among the most hydrous examples. Although the list of anhydrous minerals containing structurally bound OH continues to grow, greater emphasis on quantitative analysis is needed in constraining water in the mantle (*10*). In this article, we report measurements of concentrations of this form of hydrogen in minerals and rocks from Earth's mantle and discuss the implications for the geochemistry of water in Earth's interior.

The Problem of Water in the Mantle

Determination of Earth's water budget and the identification of suitable repositories for H (colloquially "water") in the mantle are long-standing problems in geology with important implications for the evolution of the planet as a whole. An early conclusion that the oceans and atmosphere have accumulated throughout Earth's history by progressive degassing of the interior (*11*) drew attention to the need for suitable storage sites for water in the mantle. More recent studies have implicated early catastrophic degassing (*12*), possibly contemporaneous with accretion (*13*), in the formation of the atmosphere and oceans, and the importance of recycling (*14*) in the geochemical cycles of Earth's volatile constituents. Because of the important role of the mantle in degassing and recycling processes, an appreciation of the concentrations and chemical speciation of these volatile components in the mantle is imperative if we are to understand the evolutionary history of the atmospheres and oceans and their links to reservoirs of volatiles in Earth's interior.

The variable but ubiquitous occurrence of water in mantle-derived magmas, and the occurrence of hydrous minerals such as mica and amphibole in samples of the mantle brought up as xenoliths in volcanic eruptions, testify to the presence of water in the upper mantle. This water can be present as OH in minerals or as a free vapor phase or can be dissolved in a silicate or carbonate melt (*15*). Among the candidate mineral phases for water storage in the mantle are a number of dense, OH-bearing magnesium silicates that either have been synthesized in high-pressure experiments (*16*) or have been predicted to occur on the basis of crystal-structure systematics (*17*). However, it remains to be demonstrated that these phases would be stable under the temperature and bulk compositions prevailing in the upper mantle. In addition to these stoichiometrically hydrous minerals, the β-spinel polymorph of Mg_2SiO_4 has also been proposed as a possible repository for mantle water (*18*).

Importance of Structural OH in the Mantle

The water contained in minerals with OH as an essential structural component, such as micas and clay minerals, dominates the water content of most crustal rocks, because the concentrations of OH in these minerals are typically orders of magnitude greater than those in

---

The authors are in the Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125.

Table 1. Nominally anhydrous, rock-forming minerals in which the occurrence of OH or H_2O has been demonstrated.

- Andalusite
- Cordierite
- Feldspars
  - Sanidine
  - Orthoclase
  - Microcline
  - Plagioclase
- Garnets
  - Almandine
  - Andradite
  - Grossular
  - Pyrope
  - Spessartine
- Kyanite
- Nepheline
- Olivine
- Clinopyroxenes
  - Aegirine
  - Augite
  - Diopside
  - Hedenbergite
  - Omphacite
- Orthopyroxene
  - Enstatite
- Quartz
- Rutile
- Scapolite
- Sillimanite
- Titanite
- Zircon

the nominally anhydrous minerals. However, because of the volatility of water, these stoichiometrically hydrous minerals break down to anhydrous minerals plus a free vapor phase at the high temperatures of most of the mantle. Although the stability ranges of some hydrous minerals, such sodium- or potassium-bearing amphiboles and micas persist into the mantle, their abundance, and hence their water-storing capacity, is limited by the low alkali content of average mantle rocks. In contrast, nominally anhydrous, OH-bearing minerals such as pyroxenes, olivine, and garnet, which probably make up most of the upper mantle, have a wide pressure-temperature stability range and no special compositional requirements. Their relative importance as repositories of mantle H may therefore be considerable.

In addition to the global geochemical consequences, OH in minerals of major abundance, such as olivine, appears to have important implications for the physical properties of planetary mantles, and several recent studies have addressed the effects of water and OH on the rheology of olivine (*19*). The presence of hydrogen in olivine has also been proposed to account for the electrical conductivity of Earth's upper mantle (*20*).

Initial indications of the potential importance of OH substitution in anhydrous mantle minerals were provided by both experimental (*21*) and theoretical (*22, 23*) investigations. The known replacement of SiO_4 by $(OH)_4$ in garnets of the hydrogrossular series provided an attractive substitutional mechanism (the "hydrogarnet substitution") for OH incorporation in all the anhydrous silicates, and several workers (*22, 24*) suggested that this process played an important role in the mantle. The importance of this substitution for mantle water was questioned by others (*23, 25*), however, and multiple substitutional mechanisms for H are indicated for many natural garnets on IR spectroscopic and other grounds (*26, 27*). These probably include substitution of single OH groups for O anions, the mechanism suggested by Martin and Donnay (*23*) to be important for water storage in the mantle.

Despite the numerous conjectures, few studies of the water contents of actual mantle rocks have been attempted, and our best current measurements of mantle water abundances (a few hundred parts per million) come from studies of mantle melting products in the form of quenched submarine basaltic glasses (*28–30*). However, these studies are rarely, if ever, able to identify the host phase for water in the mantle.

Concentrations of Structural OH in Mantle Minerals

A number of studies have reported IR data on OH (or lack thereof) in individual minerals of mantle origin. These include garnet (*31–33*), olivine (*34, 35*), pyroxenes (*36, 37*), kyanite (*38–40*), rutile (*39–41*), zircon (*42*), corundum, sanidine, and coesite (*39*), and H in diamond (*43*). We determined OH concentrations in 216 mineral samples of mantle origin by IR spectroscopy (Fig. 1). The sample preparation and IR spectroscopic procedures follow methods outlined previously (*31, 35, 36*). Almost all samples are from xenoliths of mantle rocks in kimberlites and alkali basalts. To supplement these data, we have compiled 115 (53 mantle-derived and 62 crustal samples) determinations of OH concentration from the literature, some of which we have revised using the preferred set of calibrations [see (*10*)]. The concentration data (Fig. 2) show that OH abundances in nominally anhydrous mantle minerals from different petrological environments (rock types) range from less than 1 ppm to on the order of 1000 ppm H_2O.

The large number of garnets (185) reveals a wide range of OH concentrations (<1 to 200 ppm H_2O), with most containing less than 60 ppm H_2O. The OH contents display a number of interesting petrological correlations (*33*), including our confirmation of the observation (*32*) that garnets from the mantle beneath the Colorado

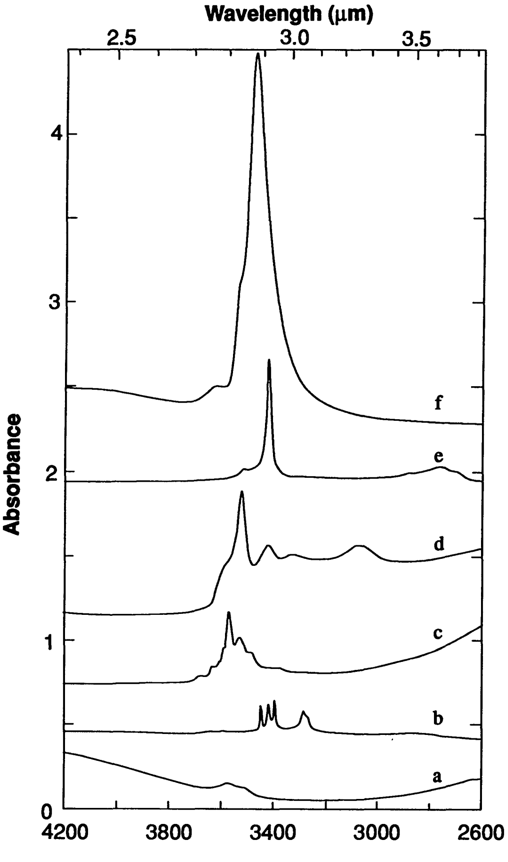

Fig. 1. Representative IR spectra of mantle minerals in the OH stretching region. All spectra were normalized to 1-mm sample thickness. The positive features between 3000 and 3800 cm^{-1} correspond to stretching vibrations of OH in the mineral structures, and their intensities are approximately proportional to the OH concentration. Broad absorptions between 3800 and 4200 cm^{-1} are due to electronic transitions in Fe^{2+}, and features at frequencies less than 2600 cm^{-1} arise from overtones of fundamental Si–O vibrations. Curve a, garnet MON-9, Monastery, South Africa, unpolarized; curve b, kyanite GRR-343, Rietfontein, South Africa, (100) section, unpolarized; curve c, olivine ROM250-OL26, Monastery, South Africa, unpolarized; curve d, enstatite PMR-54, Premier, South Africa, (100) section, polarized parallel to [001]; curve e, zircon KLV-33.R, Kaalvallei, South Africa, polarized parallel to [001]; curve f, omphacite HRV147, Roberts Victor Mine, South Africa, polarized parallel to gamma (the principal vibration direction of highest refractive index).

Plateau of the southwestern United States have OH contents that are invariably more hydrous (by about a factor of 2) than garnets from the mantle regions below southern Africa.

All orthopyroxenes analyzed contain significant amounts of OH, with most falling in the range of 100 to 450 ppm. The highest OH concentrations are recorded in orthopyroxenes from coarse-grained garnet peridotites, which may have reacted with hydrous fluids in the mantle (metasomatism). In addition to OH in the pyroxene structure reported in Table 2, the IR spectra of these orthopyroxenes indicate the presence of OH in amphibole lamellae.

Clinopyroxenes of varying composition, including diopsides, omphacites, and augites, are all significantly OH-bearing, and omphacites, particularly those with cation vacancies (*37*), display the greatest OH absorption intensities (*44*). The greatest OH concentration in a mantle diopside (about 580 ppm H_2O) was observed in a Cr-rich megacryst from Kimberley, South Africa. Clinopyroxene is typically the most OH-rich mineral of major volumetric importance in the mantle rocks studied.

Olivines show a considerable range in OH concentration (<1 to >100 ppm H_2O). Olivines from garnet peridotites typically contain more OH than those from spinel lherzolites (*45*). The highest OH content found to date in a mantle olivine is from an Fe-rich olivine megacryst from the Monastery kimberlite, South Africa (Fig. 1, curve c) (*46*).

Some phases apparently incorporate very little OH. We have detected no OH in spinels from spinel peridotites and two alkremites (garnet + spinel ± corundum rocks), but detection limits are high because of interference from absorptions due to tetrahedral Fe^{2+} in the OH region. An earlier study (*39*) detected no OH in coesite or corundum, and we have confirmed this result on corundum from eclogites and an alkremite.

Among the other accessory phases, rutile exhibits extremely strong OH absorptions, particularly in those samples from highly metasomatized environments (*41*) that are rich in hydrous minerals. Our and other (*39*) data on rutile in eclogite suggest that this phase can accommodate considerable amounts of OH, although its modal abundance is usually less than 1%. The apparently high OH contents of rutile suggest that its structural analog, stishovite, may be similarly hydrous and act as a possible H reservoir, if it occurs in the mantle. Zircon, which is believed to belong to the megacryst suite (*48*), an assemblage of coarsely crystalline minerals probably formed by crystallization of a magma at high pressure, is routinely hydrous at the 50 to 100 ppm level, but its rarity in the mantle

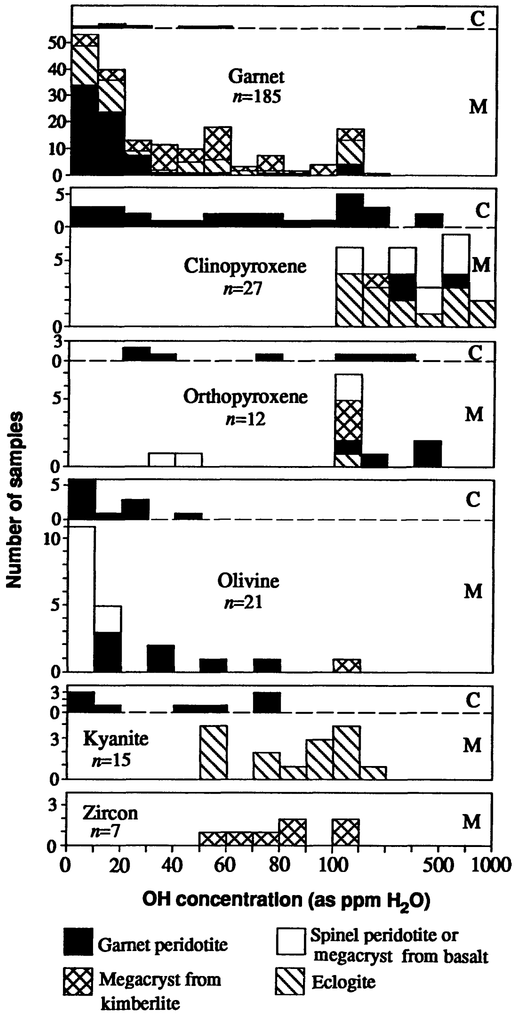

Fig. 2. Range of OH contents of mantle minerals, expressed as ppm H_2O. Note change in concentration scale at 100 and 500 ppm. For each mineral, the corresponding range of OH contents in crustally derived samples is displayed for comparison; C and M refer to crustal- and mantle-derived samples, respectively, and *n* is the number of mantle mineral analyses reported. Data from this work (216 analyses) and from the literature (115 analyses). Sources of data: garnets (*31, 32*); clinopyroxenes (*8, 36, 37, 70*); orthopyroxenes (*36*); olivines (*35*); kyanite (*38, 39*); zircon (*42*). Key to the host rock types applies only to mantle samples.

Table 2. Water concentrations in anhydrous minerals in mantle xenoliths. Abbreviations: cpx, clinopyroxene; gt, garnet; ky, kyanite; ol, olivine; opx, orthopyroxene; sp, spinel Whole rock OH concentrations calculated from observed mineral proportions and OH concentrations.

Sample	Rock type	Locality	OH concentrations (ppm H_2O)				
			Ol	Opx	Cpx	Gt	Whole rock
KBH-1	Sp lherzolite	Kilbourne Hole, NM	3	186	530		105
KBH-9	Sp lherzolite	Kilbourne Hole, NM	3	180	490		100
WKR	Sp lherzolite	West Kettle River, BC	<1	50	150		28
KOH-29	Gt lherzolite	Koherab, Namibia	10	180	370	<5	70
JJG1738	Gt lherzolite	Jagersfontein, SA	55	400	[600]*	7	175
PMR-50	Gt lherzolite	Premier, SA	17	210	[500]†	15	80
BFT-20	Gt harzburgite	Kimberley, SA	79	460		6	125
JAG-18	Gt websterite	Jagersfontein, SA		200	500	5	260
HRV-147	Eclogite	Roberts Victor, SA			470	4	235
RFT-2	Ky eclogite	Rietfontein, SA			1080	51	565
Primitive mantle‡	Sp lherzolite		140	460	590		290
Primitive mantle‡	Gt lherzolite		140	460	590	200	245

*OH in clinopyroxene detected by IR spectroscopy but difficult to quantify because of spectral interference from other features believed due to amphibole lamellae. The concentration assigned is equivalent to the maximum observed in mantle Cr-diopside and is a probable minimum for the sample, given the OH partitioning observed between orthopyroxene and clinopyroxene in other rocks. †OH in clinopyroxene not measured, but assigned on the basis of opx-cpx partitioning. ‡Mineral proportions from McDonough (*56*); OH concentrations are the maximum observed in each mineral (see text for discussion).

renders it of little consequence for storing significant amounts of OH. Kyanite exhibits a range of OH contents, from 50 to 200 ppm, which is correlated with host rock type (*40*).

Stability of OH in minerals during transport from the mantle to the surface. An unresolved issue is the degree to which the OH contents of nominally anhydrous minerals are perturbed during their transport to the surface in volcanic eruptions. It is possible that some H has been lost by oxidation reactions (*49*), such as occur in amphiboles (*50*), particularly in the samples that were contained in basalt flows. At the present stage, we cannot rule out the possibility that the OH contents of some mineral samples have been perturbed to some degree by processes that occur after the materials have left the mantle. On the other hand, the numerous correlations of mineral water content with petrological environment (xenolith type) for samples with similar transport and eruption histories suggest that source information is preserved. The stability of the hydrous component in synthetic pyrope has been demonstrated up to 50 kbar and 1100°C (*51*). More studies on the OH content of synthetic and natural minerals equilibrated under known conditions are required to evaluate the stability of the hydrous components and their kinetic response to changes in external conditions.

The Water Content of the Mantle

Mantle peridotites. We have calculated the OH concentrations in the anhydrous mineral fractions of seven peridotites and four eclogites by analysis of their constituent phases and modal proportions. Details of the mineral concentrations and assumptions made, together with the calculated concentrations, are reported in Table 2. In peridotites, these range from 28 ppm H_2O in a spinel lherzolite from West Kettle River, British Columbia, to 175 ppm in a coarse-grained garnet lherzolite from Jagersfontein, South Africa. Many of the samples are derived from the lithospheric mantle beneath continents, which has had a complex geological history, and it is thus not clear how representative these samples are of the upper mantle. Nevertheless, the data indicate that the nominally anhydrous minerals in this region of the mantle can hold at least 175 ppm H_2O.

In many kimberlite-derived, coarse-grained garnet lherzolites the OH in anhydrous minerals may be subordinate to water bound in phlogopite and amphiboles, which are relatively common hydrous phases. However, these hydrous minerals are unevenly distributed, and where they are absent the water concentrations reported here may represent something close to the total water content of the peridotitic continental upper mantle. The much higher OH concentrations in peridotitic garnets from the Colorado Plateau suggest that water concentrations may be particularly high in some regions of the subcontinental mantle. Hydrous minerals are common in mantle samples from this region (*52*), and the inferred high water content of this region of the mantle is possibly related to the subduction of wet oceanic lithosphere at a shallow angle beneath western North America during the late Cretaceous and early Tertiary (*53*).

High-temperature deformed garnet peridotites from kimberlites typically do not contain primary hydrous minerals, and most of their water budget is probably held in anhydrous minerals, although fluid and melt inclusions may play a role (*54*). These peridotites appear to be related to the megacrysts in kimberlites (*55*), possibly having equilibrated to variable degrees with the hydrous megacryst magmas that are rich in incompatible elements. Thus these peridotites and the kimberlite-hosted megacrysts may represent local areas of increased water activity.

Water in the depleted upper mantle (MORB source region). Recent estimates of mantle water contents from basalt glasses (*29, 30*) are in the range of 100 to 200 ppm H_2O for a normal mid-ocean ridge basalt (N-MORB) source. This amounts to approximately 10% of the present ocean mass, if this source region is assigned to the upper 670 km of the mantle. The data in Table 2 show that the minerals olivine, orthopyroxene, clinopyroxene, and garnet, which probably constitute much of this source region, can accommodate most or all of this water. If we reconstitute a spinel or garnet lherzolite using estimates of the modal abundances in primitive upper mantle (*56*) and assign to each mineral the greatest OH abundance measured in this study (an indication of the minimum possible saturation level for OH in these phases), then the resulting concentrations of 245 ppm H_2O (garnet lherzolite) or 290 ppm H_2O (spinel lherzolite) suggest that it is possible to contain all the water in the N-MORB source in the nominally anhydrous minerals.

If N-MORB is produced by between 5 and 25% melting of peridotite and we assume a bulk distribution coefficient for water between basalt and solid residue of 0.01 (*57*), then the residual peridotite after basalt extraction is predicted to contain in the vicinity of 5 to 35 ppm H_2O. The higher concentrations measured in most of our samples suggest that these rocks are either residues of more hydrous partial melting events, such as might be expected above subduction zones, or have seen later introduction of H. The lowest peridotite OH contents (28 ppm H_2O) were observed in a spinel lherzolite xenolith from the West Kettle River, British Columbia. Xenoliths from this locality are believed to have originated in the oceanic mantle (*58*), and our sample WKR may represent a region of the mantle that has been little influenced by later hydrous processes.

Water in undepleted or enriched mantle. The water contents of relatively undifferentiated basaltic magmas of ocean islands such as Hawaii and enriched (E-type) MORB are typically higher than those of N-MORB and have been estimated to be in the region of 0.35% (*29, 59*). For a distribution coefficient of ~0.01 for water and 5 to 15% partial melting, the water content of this source region is calculated to be in the range of 200 to 550 ppm and is rather insensitive to the precise value of the assigned distribution coefficient for water, so long as it is $\ll 1$. This range agrees with a previous estimate of 250 to 450 ppm for E-MORB source mantle (*30*). The accommodation of this much water in upper mantle anhydrous minerals would depend on OH solubilities higher than have been demonstrated in this study. It has been argued that hydrous minerals (*60*) or fluids (*61*) are present in the source regions of Hawaii, which suggests that the anhydrous minerals may become saturated in OH at bulk water concentrations in this range.

With the maximum measured OH contents in the anhydrous minerals, an amount of water equivalent to 85% of the current ocean mass can be accommodated in the whole mantle. Alternatively, if the oceans were in fact derived from the mantle (which is not established) and originated from that portion modeled to have degassed to yield Earth's atmosphere [about 46% (*12*)], then these maximum observed OH concentrations suggest that up to 40% of the present ocean could originally have been stored in this form. However, it should be stressed that these measured OH concentrations do not provide strong constraints on the upper bounds for water storage in minerals because of the unknown effects of pressure on H solubilities.

Implications for Mantle Processes

Melting and degassing. The comparatively high OH concentrations recorded in pyroxenes are in accord with observations (*27, 28*) that a small amount of water is retained in the solid mantle after partial melting and extraction of ocean-ridge basalts. The strong preference of OH for both orthopyroxene (opx) and clinopyroxene (cpx) over olivine (ol) measured in most xenoliths implies that the behavior of water during mantle melting will be governed by the [opx + cpx]/[ol] ratio. In contrast, most other incompatible trace elements, such as K, Rb, Ba, U, and the rare-earth elements reside in clinopyroxene or garnet (gt), and their fractionation during melting is determined by the [cpx + gt]/[opx + ol] ratio. Because garnet and clinopyroxene preferentially enter the liquid phase during partial melting, H should be retained in the solid residue to a greater extent than many other incompatible trace elements. This effect is enhanced at high degrees of partial melting, where the only solid phases remaining are orthopyroxene and olivine. The OH concentrations observed in pyroxenes provide an explanation for the relative compatibility of H_2O [more compatible than K, Rb, Nb, Cl, and La, but less compatible than Zr, Ti, Y, and Nd (*30*)] during MORB genesis. These relations suggest that the depletion rate of water from the mantle by melting, eruption, and degassing of basalt is slightly slower relative to that of other elements with high incompatibility.

Distribution of hydrous phases in the mantle. Figure 3 depicts the predicted principal host phases for water in a peridotitic upper mantle, if we assume that the OH concentrations measured in the most OH-rich minerals are close to saturation levels for these phases under general upper mantle conditions. The uncertainty in this assumption may result in some shift in the magnitude of the nominally anhydrous mineral field in Fig. 3, as the variation of OH solubility in these minerals under mantle conditions becomes established.

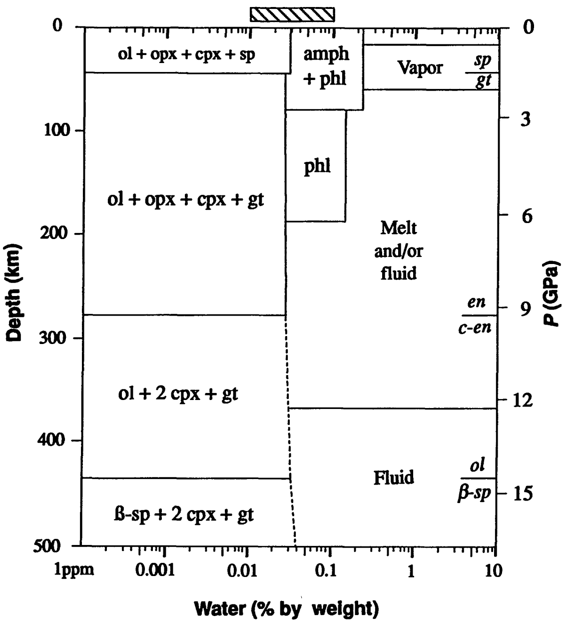

Fig. 3. Diagram showing the proposed major repositories of H in peridotitic upper mantle with increasing degree of hydration, as a function of pressure. The temperature-depth profile assumed here corresponds approximately to an oceanic geotherm. The range of estimated water contents in the upper mantle is shown by the hatched bar on top. Nominally anhydrous minerals are estimated to accommodate up to about 300 ppm H_2O in the bulk rock before saturation with hydrous minerals (at lower pressures) or a liquid phase (at high pressures). The maximum amounts of water that can be stored in amphiboles and micas are limited by the alkali content of the bulk rock, which here corresponds to the values of Jagoutz *et al.* (*71*) for primitive mantle. The fields of melt and fluid are defined by the intersection of the solidus for peridotite-H_2O with the temperature-depth profile (geotherm) chosen. In addition to the phases illustrated here, it has been suggested (*72*) that the synthetic hydrous minerals such as phase A ($Mg_7Si_2O_{14}H_6$) and phase B ($Mg_{12}Si_4O_{21}H_2$) play a role in water-bearing mantle. However, their thermal stability at normal mantle temperatures and in appropriate bulk compositions has been questioned (*73*). In regions of the mantle colder than the average, such as encountered in a downgoing slab, the phase boundaries for the stoichiometrically hydrous minerals, as well as the onset of melting, are displaced to higher pressures, and hydrous phases, such as brucite, the humite group minerals, phase A, and phase B may be stable at a range of pressures, particularly in the olivine-rich bulk compositions that are expected to be generated by melting and extraction of ocean-ridge basalt. Abbreviations: ol, olivine; opx, orthopyroxene; cpx, clinopyroxene; gt, garnet; sp, spinel; en, enstatite (magnesian orthopyroxene); c-en, magnesian monoclinic pyroxene; β-sp, beta-spinel polymorph of olivine (Mg_2SiO_4); amph, amphibole; phl, phlogopite. Labeled tics on the right ordinate indicate pressure-induced phase changes in the solid mantle mineral assemblage. High-pressure solid phase relations are from Gasparik (*74*).

Because only the upper 150 km or so of the mantle (with rare exceptions) is represented in xenolith suites, the OH contents of minerals of deeper origin cannot be measured directly. Although no firm conclusions can be drawn at this stage, general trends in our data suggest that the OH concentration in some anhydrous minerals increases at higher pressures. The far lower OH content of pyrope garnets than both orthopyroxenes and clinopyroxenes suggests that, as increasing amounts of pyroxene become dissolved in the garnet structure with depth in the mantle, the solubility of OH in the anhydrous minerals may be reduced. However, the proposed transformation of olivine to β-Mg_2SiO_4 near a depth of 400 km (*62*) may increase the water-carrying capacity of nominally anhydrous minerals in the transition zone. The estimates of OH solubility in nominally anhydrous minerals suggest that stoichiometrically hydrous, high-pressure phases (the so-called dense hydrous magnesium silicates) are not required to be present in the depleted upper mantle. There may be exceptions where the mantle has been hydrated by, for example, proximity to a dehydrating lithospheric plate in a subduction zone or contamination in the neighborhood of a plume.

The local distribution of hydrous phases is further complicated by the capability of water-rich fluids to transport alkali metals such as Na and K. Thus, hydrous minerals with appreciable high temperature and pressure stability, such as F-bearing potassic richterite (*63*), and possibly phlogopite, may be locally concentrated where alkali and halogen concentrations are elevated along with water.

Water recycling. Lithospheric plates returned to the mantle at subduction zones are water-rich in their upper regions because of their interaction with the hydrosphere. However, most water held in the subducting slab will be released on compression of pore space and when hydrous minerals such as opal, zeolites, clays, chlorite, serpentine, and amphibole undergo dehydration reactions (*64*). It has been predicted that almost all water originally present in the oceanic crust will be prevented from entering the deep mantle because of these dehydration reactions. However, the oceanic crust transforms to eclogite, a roughly 50-50 mix of garnet and omphacitic clinopyroxene, in response to increasing pressure during subduction. Our studies of mantle eclogites reveal that, although most high-pressure eclogitic garnets are OH-poor, the omphacitic pyroxenes in these rocks contain comparatively large amounts of OH. Thus deep subduction of omphacitic pyroxene, perhaps supplemented by the accessory minerals rutile and kyanite, may allow the transport of water (up to about 500 ppm) into deep regions of the mantle. Pods of eclogite situated in peridotitic mantle may form local areas of comparatively high water concentration, at least as far as the nominally anhydrous minerals are concerned, and such material may contribute to the source region of ocean island basalts (*65*).

It is commonly held that some water derived from dehydration of the subducting slab infiltrates the overlying mantle wedge, where it has been implicated in partial melting processes that give rise to arc magmas (*66*). The comparatively water-rich nature of primary arc basalts [1 to 2% by weight (*67*)] suggests that their solid mantle residues may contain up to 200 ppm or so of water, bound in nominally anhydrous minerals, and that there may be regions of the mantle wedge where nominally anhydrous minerals are saturated in OH. The fate of this hydrated peridotite is not known, but it may end up in the continental lithosphere, remain in the shallow mantle, or be dragged into the deep mantle by the descending slab.

Although the response of the hydrous component of the nominally anhydrous minerals to increases in temperature and pressure is poorly known at present, there is the possibility that H bound in this form can survive transport to considerable depths. Because peridotite is believed to flow continuously through the mantle wedge above a subduction zone (*66, 68*), this material can be continually hydrated and either recycled into deeper regions of the mantle or contribute to a hydrated uppermost mantle. The water content predicted for the nominally anhydrous minerals in the hydrated mantle wedge appears to be sufficient to account for that of the MORB source region. The continuous conveyor belt of OH-saturated, but nominally anhydrous, peridotite above subduction zones may contribute to steady-state recycling of water through the upper regions of Earth, a process inferred on the basis of the uniformity of primary hydrogen isotope compositions of igneous rocks to be important in Earth's water cycle (*69*).

REFERENCES AND NOTES

1. Geological literature is generally not precise in its designation of the element hydrogen in the mantle. The term "water" is commonly used to encompass all chemical forms of hydrogen, perhaps with the implied assumption of the oxidized form of the element. In this article we follow this loose usage in referring to OH bound in minerals as one form of mantle "water." Although the H occurs as OH in the minerals of this study and is detected as such by IR spectroscopy, we follow the convention for other elements in reporting analyses of H in terms of the charge-balanced oxide, H_2O (by weight).
2. J. R. Goldsmith, *Contrib. Mineral. Petrol.* **95**, 311 (1987).
3. A. K. Ganguli, A. J. Vega, R. D. Shannon, G. R. Rossman, in preparation.
4. G. R. Rossman and G. C. Solomon, in preparation.
5. A. M. Hofmeister and G. R. Rossman, *Am. Mineral.* **70**, 794 (1985).
6. D. T. Griggs and J. D. Blacic, *Science* **147**, 292 (1965).
7. A. Kats, *Philips Res. Rep.* **17**, 133 (1962); R. D. Aines, S. H. Kirby, G. R. Rossman, *Phys. Chem. Minerals* **11**, 204 (1984).
8. R. W. T. Wilkins and W. Sabine, *Am. Mineral.* **58**, 508 (1973).
9. R. D. Aines and G. R. Rossman, *J. Geophys. Res.* **89**, 4059 (1984); G. R. Rossman, *Rev. Mineral.* **18**, 193 (1988).
10. The difficulty of reliable and accurate quantitative calibration compared with the relative ease and intriguing variability of the IR measurements has caused the determination of absolute concentrations to lag somewhat behind the descriptive studies. Many studies have used the generic calibration developed by M. S. Paterson [*Bull. Mineral.* **105**, 20 (1982)], but it has become apparent that this is not (and was not intended to be) suitable for rigorously quantitative analysis of OH in minerals. Progress toward accurate mineral-specific calibrations has been evolutionary, with consecutive calibration studies often generating progressively lower estimates of H concentration as the analytical technology improves. The convergence of results from recent manometric measurements (D. R. Bell, P. D. Ihinger, G. R. Rossman, S. Epstein, in preparation) and those from nuclear reaction analysis [D. Kuhn, F. Rauch, H. Baumann, *Nucl. Instrum. Methods B* **45**, 252 (1990); unpublished data] provides the basis for most calibrations used here. The calibrations for Ca- and Mg-rich garnets agree within uncertainty, but pyroxene calibrations are based on precise analysis of single samples and have not been tested on a variety of mineral compositions. We estimate that the uncertainty in the accuracy of the measured OH contents of most minerals is on the order of a few tens of percent relative.
11. W. W. Rubey, *Geol. Soc. Am. Bull.* **62**, 1111 (1951).
12. C. J. Allegre, T. Staudacher, P. Sarda, *Earth Planet. Sci. Lett.* **81**, 127 (1987).
13. Y. Abe and T. Matsui, *Proc. Lunar Planet. Sci. Conf.* **17**, E291 (1986).
14. H. D. Holland, *The Chemical Evolution of the Atmosphere and Oceans* (Princeton Univ. Press, Princeton, NJ, 1984); G. Schubert, D. L. Turcotte, S. C. Solomon, N. H. Sleep, in *Origin and Evolution of Planetary and Satellite Atmospheres*, S. K. Atreya, J. B. Pollack, M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, 1989), pp. 450–483.
15. P. J. Wyllie, *Min. Soc. Am. Spec. Pap.* **3**, 3 (1970).
16. A. E. Ringwood and A. Major, *Earth Planet. Sci. Lett.* **22**, 130 (1967); C. B. Sclar, L. C. Carrison, C. M. Schwartz, *Trans. Am. Geophys. Union* **46**, 184 (1965).
17. L. W. Finger and C. T. Prewitt, *Geophys. Res. Lett.* **16**, 1395 (1989).
18. J. R. Smyth, *Am. Mineral.* **72**, 1051 (1987); J. W. Downs, *ibid.* **74**, 1124 (1989); T. E. Young, H. W. Green II, A. M. Hofmeister, *Eos* **72**, 144 (1991).
19. M. G. Justice, E. K. Graham, R. E. Tressler, I. S. T. Tsong, *Geophys. Res. Lett.* **9**, 1005 (1982); S. J. Mackwell, D. L. Kohlstedt, M. S. Paterson, *J. Geophys. Res.* **90**, 11319 (1985); S. Karato, M. S. Paterson, J. D. FitzGerald, *ibid.* **91**, 8151 (1986); M. R. Drury, *Phys. Chem. Minerals* **18**, 106 (1991).
20. S. Karato, *Nature* **347**, 272 (1990).
21. C. B. Sclar, L. C. Carrison, O. M. Stewart, *Trans. Am. Geophys. Union* **48**, 226 (1967).
22. W. S. Fyfe, *Phys. Earth Planet. Inter.* **3**, 196 (1970).
23. R. F. Martin and G. Donnay, *Am. Mineral.* **57**, 554 (1972).
24. L. Ackermann, L. Cemic, K. Langer, *Earth Planet. Sci. Lett.* **62**, 208 (1983).
25. G. A. Lager, T. Armbruster, F. J. Rotella, G. R. Rossman, *Am. Mineral.* **74**, 840 (1989).
26. G. R. Rossman and R. D. Aines, *ibid.* **76**, 1153 (1991).
27. T. C. Birkett and W. E. Trzcienski, *Can. Mineral.* **22**, 675 (1984).
28. J. G. Moore, *Contrib. Mineral. Petrol.* **28**, 272 (1970).
29. J. E. Dixon, E. M. Stolper, J. R. Delaney, *Earth Planet. Sci. Lett.* **90**, 87 (1988).
30. P. J. Michael, *Geochim. Cosmochim. Acta* **52**, 555 (1988).
31. R. D. Aines and G. R. Rossman, *Am. Mineral.* **69**, 1116 (1984).
32. _____, *Geology* **12**, 720 (1984).
33. D. R. Bell and G. R. Rossman, *Contrib. Mineral. Petrol.*, in preparation.
34. M. Kitamura *et al.*, *Nature* **328**, 143 (1987).
35. G. H. Miller, G. R. Rossman, G. E. Harlow, *Phys. Chem. Minerals* **14**, 461 (1987).
36. H. S. Skogby, D. R. Bell, G. R. Rossman, *Am. Mineral.* **75**, 764 (1990).
37. J. R. Smyth, D. R. Bell, G. R. Rossman, *Nature* **351**, 732 (1991).
38. A. Beran and M. A. Götzinger, *Mineral. Petrol.* **36**, 41 (1987).
39. G. R. Rossman and J. R. Smyth, *Am. Mineral.* **75**, 775 (1990); V. M. F. Hammer and A. Beran, *Mineral. Petrol.* **45**, 1 (1991).
40. D. R. Bell and G. R. Rossman, *Eos* **71**, 523 (1990).
41. D. Vlassopoulos, G. R. Rossman, S. E. Haggerty, *ibid.*, p. 626.
42. J. A. Woodhead, G. R. Rossman, A. P. Thomas, *Am. Mineral.* **76**, 1533 (1991).
43. E. Fritsch, K. Scarratt, A. Collins, in *New Diamond Science and Technology, Materials Research Society International Conference Proceedings 1990*, R. Messier, J. T. Glass, J. E. Butler, R. Roy, Eds. (Materials Research Society, Pittsburgh, 1991), pp. 671–676; O. Navon, I. D. Hutcheon, G. R. Rossman, G. J. Wasserburg, *Nature* **335**, 784 (1988).
44. Although the large IR absorptions observed in omphacite pyroxenes (solid solutions of primarily the diopside and jadeite end-members) suggest that they commonly have the greatest OH concentrations among mantle-derived pyroxenes, the OH IR spectra of jadeite-rich omphacites differ from those of diopside and augite pyroxenes in the number and frequency of the OH absorptions [see (*36*)]. This difference prompts caution in the application of the present calibration of the OH spectrum of clinopyroxene (based on augitic diopside) and indicates some uncertainty in the analysis of OH in omphacitic pyroxenes. On the basis of systematics in the relation between absorption coefficient and band energy of amphiboles [H. S. Skogby and G. R. Rossman, *Phys. Chem. Minerals* **18**, 64 (1991)], it is suggested (D. R. Bell, P. D. Ihinger, G. R. Rossman, S. Epstein, in preparation) that this calibration may overestimate the OH contents of jadeite-rich omphacites by about 30%.
45. Because garnet lherzolites derive from greater depths than spinel lherzolites (see Fig. 3), the higher OH contents observed in olivines from garnet lherzolites may indicate a pressure effect on OH solubility in olivine. However, the garnet peridotites were transported to the surface in volatile-rich kimberlites, whereas all spinel lherzolites studied here derive from basalts and may have suffered some dehydration.
46. Olivine is currently the least well-calibrated mineral in terms of quantitative OH analysis. Earlier workers (*35, 47*) have used the calibration of Paterson [see (*10*)], and we have applied a similar method here. It is worth noting that this calibration tends to give lower OH contents when applied to pyroxenes and garnet than the mineral-specific calibrations. In spite of the uncertainties in calibration, the difference in the OH absorption intensity between pyroxenes and most olivines is marked (up to three orders of magnitude in integrated absorbance), and we feel confident in concluding that pyroxenes are significantly more hydrous.
47. S. J. Mackwell and D. L. Kohlstedt, *J. Geophys. Res.* **95**, 5079 (1990).
48. P. Kresten, P. Fels, G. Berggren, *Mineral. Deposita* **10**, 47 (1975); R. O. Moore, thesis, University of Cape Town (1986).
49. It has been argued (*47*) that the OH content of mantle-derived olivines will decrease as the ambient H_2 fugacity drops with decreasing total pressure during eruption. This is possible because of the very rapid diffusion of H in olivine and the reversible redox reaction involving an Fe^{2+}/Fe^{3+} couple. A similar reaction has been proposed for dehydroxylation of pyroxenes in air [H. S. Skogby and G. R. Rossman, *Am. Mineral.* **74**, 1059 (1989)]. This rapid diffusion of H is contrasted with the much slower diffusivity of possible OH defect sites in olivine and implies that the ultimate solubility of H, that is, the "OH-carrying capacity" of the mineral, is relatively unaffected during transport. If OH is lost upon eruption as suggested by Mackwell and Kohlstedt (*47*), then the measured OH concentrations are most likely underestimates of concentrations in the mantle.
50. V. E. Barnes, *Am. Mineral.* **15**, 393 (1930); M. W. Phillips, J. E. Draheim, R. K. Popp, C. A. Clowe, A. A. Pinkerton, *ibid.* **74**, 764 (1989).
51. C. A. Geiger, K. Langer, D. R. Bell, G. R. Rossman, B. Winkler, *ibid.* **76**, 49 (1991).
52. T. R. McGetchin and L. T. Silver, *J. Geophys. Res.* **77**, 7022 (1972); D. Smith, in *The Mantle Sample: Inclusions in Kimberlites and Other Volcanics*, F. R. Boyd and H. O. A. Meyer, Eds. (American Geophysical Union, Washington, DC, 1979), pp. 345–356.
53. H. H. Helmstaedt and R. Doig, *Phys. Chem. Earth* **9**, 95 (1975); P. Bird, *Tectonics* **3**, 741 (1984).
54. M. R. Drury and H. L. M. van Roermund, *Geology* **16**, 1035 (1988).
55. P. H. Nixon and F. R. Boyd, in *Lesotho Kimberlites*, P. H. Nixon, Ed. (Lesotho National Development Corporation, Maseru, 1973), pp. 67–75; J. J. Gurney and B. Harte, *Philos. Trans. R. Soc. London A* **297**, 273 (1980).
56. W. F. McDonough, *Earth Planet. Sci. Lett.* **101**, 1 (1990).
57. The choice of partition coefficient is based on a study of the geochemistry of MORB glasses, demonstrating the similarity of partitioning behavior of water to that of La during partial melting (*29*). Some uncertainty is associated with the choice of the actual value of the partition coefficient for La [done in (*29*) on the basis of estimates from the literature], which may cause the upper estimate of 35 ppm to double. However, our calculations were done assuming batch melting, which may be unrealistic, particularly at high melt fractions, where a fractional melting model may be more appropriate. The fractional melting model would

predict water concentrations in the solid residue closer to the lower end of the given range.
58. X. Xue, H. Baadsgaard, A. J. Irving, C. M. Scarfe, *J. Geophys. Res.* **95**, 15879 (1990).
59. D. A. Clague, W. S. Weber, J. E. Dixon, *Nature*, in press.
60. D. A. Clague and F. A. Frey, *J. Petrol.* **23**, 447 (1982).
61. D. A. Clague and J. E. Dixon, *Eos* **72**, 563 (1991); J. E. Dixon, D. A. Clague, E. M. Stolper, in preparation.
62. A. E. Ringwood, *Phys. Earth Planet. Inter.* **3**, 109 (1970); C. R. Bina and B. J. Wood, *J. Geophys. Res.* **92**, 4853 (1987).
63. S. F. Foley, *Geochim. Cosmochim. Acta* **55**, 2689 (1991).
64. S. M. Peacock, *Science* **248**, 329 (1990).
65. A. W. Hoffman and W. M. White, *Earth Planet. Sci. Lett.* **57**, 421 (1982).
66. I. Kushiro, *J. Geophys. Res.* **95**, 15929 (1990).
67. M. O. Garcia, N. W. K. Liu, D. W. Muenow, *Geochim. Cosmochim. Acta* **43**, 305 (1979).
68. J. H. Davies and D. J. Stevenson, *J. Geophys. Res.*, in press.
69. H. P. Taylor, *J. Geol. Soc. London* **133**, 509 (1977).
70. J. Ingrin, K. Latrous, J. C. Doukhan, N. Doukhan, *Eur. J. Mineral.* **1**, 327 (1989).
71. E. Jagoutz *et al.*, *Proc. Lunar Planet. Sci. Conf.* **10**, 2031 (1979).
72. L. G. Liu, *Phys. Earth Planet. Inter.* **49**, 142 (1987).
73. L. W. Finger *et al.*, *Nature* **341**, 140 (1989).
74. T. Gasparik, *J. Geophys. Res.* **95**, 15751 (1990).
75. This research was supported by National Science Foundation grants EAR 88-16006 and EAR 91-04059. D.R.B. acknowledges financial support from the Harry Crossley Foundation and the American Federation of Mineralogical Societies. We thank our numerous sample donors, in particular J. J. Gurney, for their generosity, De Beers Consolidated Mines Ltd. for access to xenolith localities and collections, and G. S. Mattioli for help in the field. We are grateful to D. Endisch and F. Rauch at the University of Frankfurt for willingness to share unpublished nuclear reaction analysis data relevant to the calibrations used here. We have benefited from discussions with P. D. Ihinger, G. S. Mattioli, and E. M. Stolper, and we thank T. J. Ahrens, D. L. Anderson, J. E. Dixon, R. B. Hanson, P. J. Wyllie, and two anonymous reviewers for comments on drafts of this paper. This is Division of Geological and Planetary Sciences contribution no. 5071.

Direct Observation of Chemical Bond Dynamics on Surfaces

J. T. YATES, JR., M. D. ALVEY, M. J. DRESSER, M. A. HENDERSON, M. KISKINOVA, R. D. RAMSIER, A. SZABÓ

The dynamics of chemisorbed species as they swing to-and-fro on their adsorption sites may be directly observed with electron-stimulated desorption. The observation of the thermal disorder in adsorbate chemical bond directions, through studies of the thermal excitation of librational modes, allows one to visualize the potential energy surfaces controlling the structure and dynamics of adsorbates on single crystal metal and semiconductor surfaces. This information may be useful in understanding surface diffusion as well as the spatial aspects of surface chemical reactions.

THE BEHAVIOR OF THE CHEMICAL BONDS IN ADSORBED species is of central importance to all of surface chemistry. Indeed, the quest to understand chemical bonding at surfaces is one of the main driving forces in the field of surface science; much of current experimental and theoretical research is directed toward this general objective in one way or another. The understanding of surface bonding and reactivity has contributed immensely to the intellectual richness of the field of surface science. This knowledge has also had significant application to many diverse technologies that are controlled by surface phenomena. Among these are heterogeneous catalysis, semiconductor processing, corrosion prevention and other electrochemical technologies, many areas of materials science, and tribology.

The dynamics of molecules as they bond to a surface intimately influences the course of various thermally activated surface chemical phenomena. When a molecule interacts with a surface, the following sequence of dynamically governed events takes place: (i) adsorption from the gas; (ii) energy dissipation from the newly formed adsorbate; (iii) adsorbate libration, rotation, and vibration on its adsorption site; (iv) adsorbate diffusion with possible reaction at a neighbor site; and (v) desorption.

Modern experimental and theoretical methods of probing molecular dynamics have been applied to each of these categories of surface behavior, contributing both a classical (*1*) and a quantum mechanical (*2*) understanding of the elementary processes that determine the overall kinetics of chemical reactions on surfaces.

This article is concerned with the direct observation of the dynamics of chemisorbed species. It describes our current ability to observe the librations and rotations of chemisorbed species on their adsorption sites through the observation of the spatial patterns of thermal disorder induced in chemical bond directions. For research purposes, we select the symmetry and structure of the adsorption sites to be studied by using single crystal substrates that expose crystal planes of known structure. The substrate site structure controls the symmetry and shape of the potential energy surface that governs the motion of the thermally excited adsorbed molecules. These thermally activated motions probe the entry channels along the reaction coordinate that lead to surface diffusion and to surface reactions.

Adsorbed molecules, and also the atoms in the surface of a solid, may be studied in many ways with modern surface measurement techniques. Surface vibrational spectroscopy is one of the most powerful tools used to probe surface bonding (*3*). Information is sought about the vibrational modes and the forces coupling atoms and molecules on the surface. At the most primitive level of surface vibrational spectroscopy, observed frequencies of vibration are used as indicators of surface bond character through analogies to chemical group frequencies in molecules of known structure (*4*). More

---

J. T. Yates, Jr., and R. D. Ramsier are with the Surface Science Center, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260. M. D. Alvey is at 6385 Truman Street, Chino, CA 91710. M. J. Dresser is in the Department of Physics, Washington State University, Pullman, WA 99164. M. A. Henderson is with Battelle Northwest Laboratories, Post Office Box 999, Richland, WA 99357. M. Kiskinova is with Sincrotrone Trieste, Padiciano 99, 34012 Trieste, Italy. A. Szabó is in the Department of Chemistry, University of Washington, Seattle, WA 98195.