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Understanding interface processes and their role in the mobility of contaminants in the geosphere: The use of Surface Sensitive Techniques

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Key words: Surface analytical techniques, calcite, interface processes, surface hydration, solid-state diffusion, solid-solution formation

ABSTRACT

The composition and the quality of ground and surface waters are often controlled by the processes that take place at the interface between natural fluids and solids. Although a great deal has already been learned at the macroscopic level from classical, wet chemical and bulk solid methods, some other techniques, borrowed from physics, materials science and the computer industry can provide direct, molecular-level information from the surface and near-surface. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) provide chemical information from about the top 10 nm of powdered or solid samples. Chemical bonding data is accessible with XPS; AES allows surface chemical mapping with a resolution of about 0.1 μm . Low-energy electron diffraction (LEED) can confirm surface crystallinity and yields atomic lattice dimensions of the top few monolayers. Atomic Force Microscopy (AFM) can provide dynamic, topographic images with resolution as low as fractions of a nanometer on surfaces in air or under solution. Studies of calcite using XPS show that the dangling bonds created by cleavage are satisfied with the formation of surface hydration species, $S\text{-CaOH}$ and $S\text{-CO}_3\text{H}$ (where S represents the calcite surface). LEED and AFM data suggest a slight rearrangement of the atomic structural positions at the surface in comparison with that in bulk calcite. XPS, AES and LEED helped to prove that adsorbed divalent trace metals move into the bulk by solid-state diffusion to form a solid-solution even in dry, ultra-high vacuum conditions. AFM revealed that the calcite surface in air is highly dynamic. Surface sensitive techniques have provided new insights into the interface processes important in carbonate systems. Molecular-level understanding of these and other processes will help geochemists construct more realistic and effective models for contaminant mobility in the environment.

RESUME

La chimie des eaux de surface et des eaux souterraines est souvent contrôlée par des processus chimiques ayant lieu à l'interface entre les solides et leur environnement liquide. A côté des études macroscopiques de ces systèmes, des techniques issues de la physique, des sciences des matériaux et de l'industrie des microprocesseurs peuvent aujourd'hui fournir des informations directes, à l'échelle moléculaire de ces phénomènes d'interface. Citons par exemple la spectroscopie des électrons Auger (AES) et la spectroscopie des photoélectrons émis par rayons-X (XPS) qui permettent de sonder les dix premiers nanomètres d'une poudre ou d'un cristal. Les données concernant la nature et la force des liaisons sont disponibles grâce à XPS. Une cartographie chimique d'une surface avec une résolution horizontale de 0.1 μm environ peut être fourni par AES. La diffraction d'électrons de basse énergie (LEED) quant à elle peut être utilisée pour confirmer le degré de cristallisation d'une surface et donner les caractéristiques du réseau atomique. La microscopie à force atomique (AFM) fournit des images dynamiques topographiques avec une résolution de l'ordre du dixième de nanomètre de surfaces

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soit en solution, soit même à l'air. Des études XPS sur la calcite pure, XPS montre que les liaisons détruites suite à un clivage forment des espèces hydratées en surface du type $S\text{-CaOH}$ et $S\text{-CO}_3\text{H}$ (où S représente la surface de la calcite). AFM et LEED suggèrent un réarrangement des atomes de surface par comparaison avec leurs positions à l'intérieur du cristal. D'un autre côté, XPS, AES et LEED ont permis de montrer que les métaux traces bivalents se déplacent par diffusion en phase solide même en conditions anhydres et sous un vide poussé, pour former des phases identiques aux solutions-solides. AFM en particulier a bien démontré que la surface de la calcite à l'air est fortement instable. Tout ceci montre que ces techniques d'étude de surfaces et d'interfaces donnent de nouvelles informations sur des processus importants dans le système $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$. Une compréhension au niveau moléculaire de la chimie des surfaces devrait également aider les géochimistes à construire et proposer des modèles plus réalistes et efficaces en ce qui concerne le transport et la fixation des substances polluantes dans l'environnement.

Introduction

In the past two decades, there has been a great deal of effort to understand and model the mobility of contaminants in the geosphere. Hydrogeochemical modelling relies on physical and chemical parameters that may either be based on theory or on measurement. Often, these parameters are macroscopic and empirical. Although they can be used successfully to model contaminant behaviour in the field, accurate predictions can be difficult because macroscopic parameters linked to the system where they are measured must certainly vary in an uncharacterizable way in a heterogeneous system. It is only through understanding of the actual chemical and physical processes at the molecular level, that we can understand what macroscopic parameters to include in our models, and eventually hope to be able to predict trace element behaviour through time and space in a complex system.

In the past, physical transport models have sometimes incorporated thermodynamic and kinetic data to help describe the precipitation and dissolution of mineral phases and their control on the fluid chemistry; more recently, data describing adsorption/desorption reactions have been added. These steps have made the models more realistic, particularly for describing major component composition. Unfortunately, the behaviour of trace metals and radionuclides is often not well simulated. Because it is precisely these contaminants that are of interest to environmental scientists, we need a better way. If we could understand the reactions involving contaminant species, we would be closer to being able to predict their concentrations and then we might be able to design more effective models both at the molecular and at the ecosystem scale.

Most reactions of interest to environmental geoscientists occur at the interface of solid with fluid (liquid or gas). The solid could be particles in the air or a lake, minerals in a sediment or soil from the saturated or unsaturated zone, the scales of fish, membranes of bacteria, algae or plant debris; the fluid could be water, oil, solvents, air, other gases, or mixtures of any or all of them. Likewise, in geological environments, large scale macroscopic "processes" that determine trace element movement are controlled by the reactions that take place at the interface of mineral grains with other particles and fluids of all compositions. Analytical techniques that allow us to study only the top few nanometers of solid surfaces could provide earth scientists with valuable information about the reactions that take place at these interfaces.

Such techniques exist; they are not traditionally used for studying natural materials but they are well-known and much used in physics, materials science and the ceramics and semi-conductor industries. This short article will attempt: 1) to describe simply, four

of the many techniques that allow us to see actual surface topography on a nanometer scale and to gather direct, molecular-level, chemical and structural information from less than 10 nanometers depth into a solid surface. 2) to briefly cite a few articles published by other authors using these techniques on mineral surfaces of interest to geoscientists, 3) to present some observations of several interface processes using calcite as an example, and 4) to suggest ways in which unreliable predictions of contaminant transfer might occur if these processes are not considered in the interpretation of hydrogeochemical model results.

Surface Sensitive Techniques

There is a vast number of surface-sensitive techniques that are now available (see Hawthorne 1988 and Hochella & White 1990) and many of them are useful for studying natural materials. The four described here were chosen because they are relatively common and accessible, and together, they give complimentary information. From Auger electron spectroscopy and x-ray photoelectron spectroscopy, we gain chemical information for the top few nanometers but the latter is particularly useful for investigating chemical bonding. Low-energy electron diffraction shows the atomic structure of the top monolayers and atomic force microscopy can provide topographic images at the micro and nanometer scale. More details about these techniques can be found in Hochella 1988, Stipp 1994, Clarke 1985, Rugar & Hansma 1990, Descouts & Siegenthaler 1992, Güntherodt et al. 1994 and references cited therein. The techniques are described below.

X-ray photoelectron spectroscopy (XPS)

This technique yields energy spectra for photoelectrons that are ejected from samples by an x-ray of known wavelength. The x-ray source is often one of Mg, Al or Si with $K\alpha_{1,2}$ energy between 1,000 and 2,000 eV. The x-ray beam ejects electrons from atoms in the sample and the kinetic energy of these photoelectrons is measured in a detector (Fig. 1a). Subtraction of their kinetic energy from the known incident x-ray energy yields the binding energy with which the electron was originally held in the atom. Figure 1b shows a typical spectrum of binding energies for photoelectrons from various energy levels of the elements in a sample of freshly cleaved calcite.

X-rays deeply penetrate a sample but ejected photoelectrons lose their energy during interactions with atoms blocking their path to the surface and to the detector. Thus, depending on the sample material, there is a finite depth beyond which no photoelectrons are able to escape, and clearly, those that do are much more likely to be ejected from atoms that are in the actual surface or the top few monolayers. For this reason, XPS is a *near-surface* sensitive technique. For non-conductive minerals such as calcite, almost all photoelectrons originate from a depth of less than 10 nm or about 30 monolayers on the $\{10\bar{1}4\}$ cleavage surface. If the sample is tilted with respect to the analyzer, one can selectively exclude photoelectrons originating from deeper in the sample, thus making the technique even more surface sensitive and allowing depth resolution.

The spot size of analysis can be adjusted, but because x-rays cannot be focused, this is done with a diaphragm in front of the detector. A typical diameter of sample analysis is on

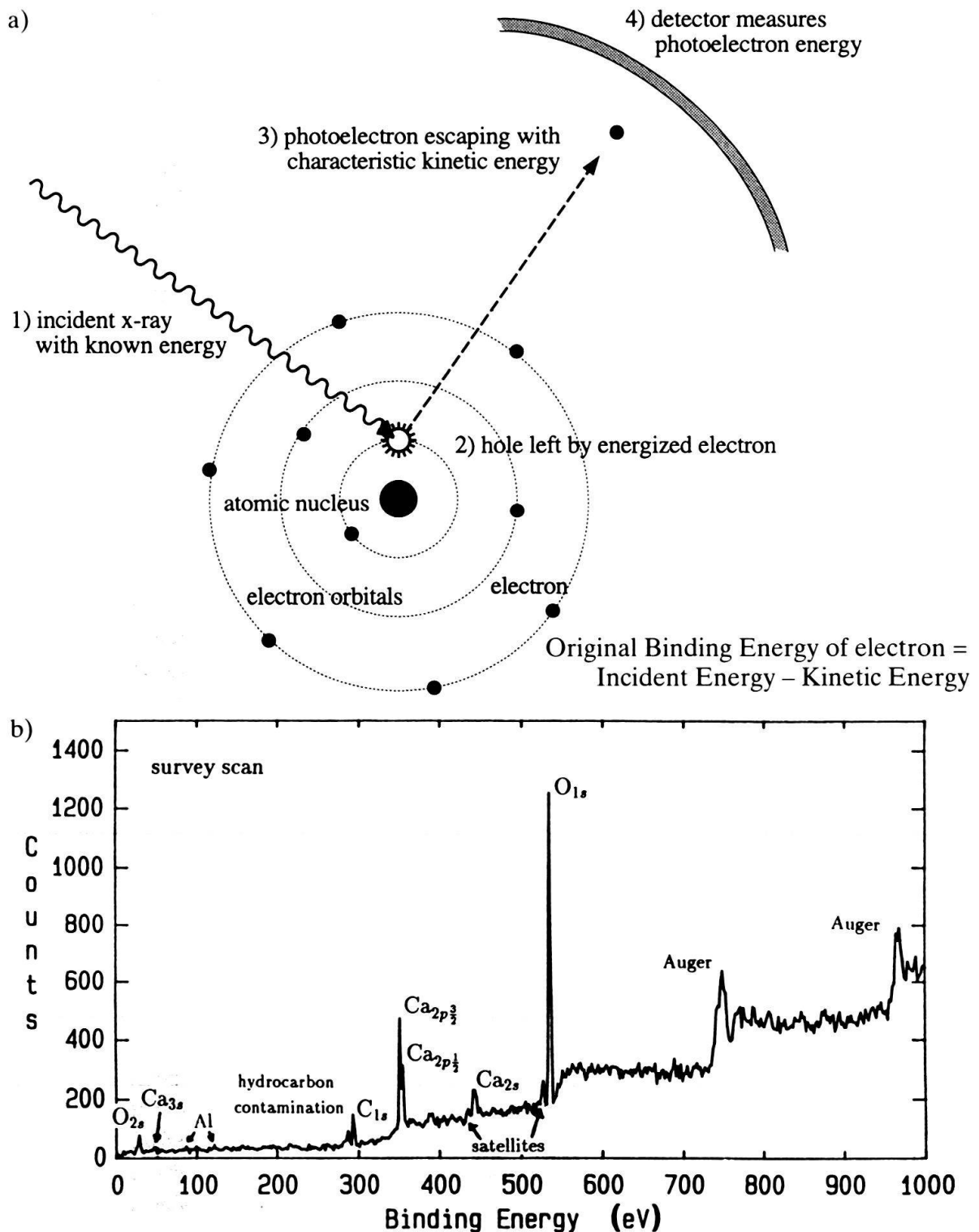


Fig. 1. a) Principles of x-ray photoelectron spectroscopy (XPS). The numbers refer to steps in the process. The technique requires ultra-high vacuum ($< 10^{-9}$ mbar). Detection limits vary with atomic number of the element analyzed and its electron configuration. Sensitivity: depth ≈ 10 nm; analysis diameter ~ 100 μm (but some new "photoelectron microscopes" have resolution of ~ 1 μm). X-ray energy: $1000 \text{ eV} < E < 2000 \text{ eV}$. Probes *near-surface*. More information about this technique can be found in Hochella (1988) or Stipp (1994) and references therein. b) A typical survey scan of a calcite cleavage surface exposed to air for less than an hour. Peaks representing all elements of CaCO_3 are present (the subscripts refer to the energy level of the photoelectron's origin); the sample holder was aluminum. Satellites result from x-rays that are not $\text{Mg K}\alpha_{1,2}$; some Auger peaks also appear.

the order of a few millimeters but resolution with state-of-the-art “photoelectron microscopes” is about 1 μm . In order to avoid loss of photoelectron intensity due to collision with gas molecules and to minimize surface contamination, XPS analyses are performed in ultra-high vacuum with pressures of 10^{-9} to 10^{-10} mbar. Although *in-situ* experiments are not possible in these conditions, we can obtain a great deal of information about bonding environments in relation to the sample’s history before its introduction to ultra-high vacuum, and sometimes we can even take advantage of this environment as will be shown later in this article.

The kinetic energy of an ejected photoelectron is a function of the strength of its original attachment in the atom. This not only varies with the element and the energy level of the electron’s origin, but it is also affected by bonds with other atoms. If an atom is involved in a tight bond with a neighbour, its valence electrons are pulled away and the core or innermost electrons will be held more tightly around its nucleus, so the binding energy of a core level photoelectron shifts slightly higher. We see this in the carbon (C_{1s}) binding energy peaks on Figure 1b. Here, electrons from carbon that are bound to oxygen in the CO_3 groups of calcite with a bond strength of 4/3 make the largest C peak, whereas singly bonded carbons from a hydrocarbon chain are observed at lower binding energy in a peak representing contamination on the surface. As electrons leave the surface, the sample acquires a positive charge, but we can correct for the effects of surface charging on insulating materials by referencing the sample to a standard. When absolute binding energies were required for the images presented in this paper, samples were referenced to a very small amount of gold ($< 5 \text{ Au atoms}/\text{\AA}^2$) that had been sputtered onto the surface.

From the XPS binding energies of peaks, atomic composition can be determined; from binding energy shifts, we can learn about atomic environments and bonding structure and from relative peak intensities, we can determine relative surface concentrations for all elements except H and He. The rather large sampling diameter makes XPS a poor choice for analyzing selected spots on a surface. The technique is sensitive to fractions of a monolayer of some adsorbed species, but detection limits vary with the atomic number of the element and its electron configuration.

Auger electron spectroscopy (AES)

This technique has many similarities to XPS and some important differences. It likewise yields electron energy spectra but in this case, they represent ejected Auger electrons. Auger electrons are emitted as a result of energy liberated when a vacancy for a core level electron is filled by an electron from a higher level. As this electron “falls” into the “hole”, its excess energy allows another electron, the “Auger” electron to escape (Fig. 2a) with kinetic energy that is characteristic of the element of origin and of the energy difference in the atomic levels involved in the interaction.

Auger analyses are carried out using the same sort of detector as is used for XPS. The intensity of AES relies on electron escape from the sample and unimpeded travel to the detector, so in order to maximize the number of electrons detected, ultra-high vacuum is used. The depth of analysis is similar to that for XPS, *i.e.* less than 10 nm for a nonconductor such as calcite. Angle-resolved analyses likewise allow depth resolution.

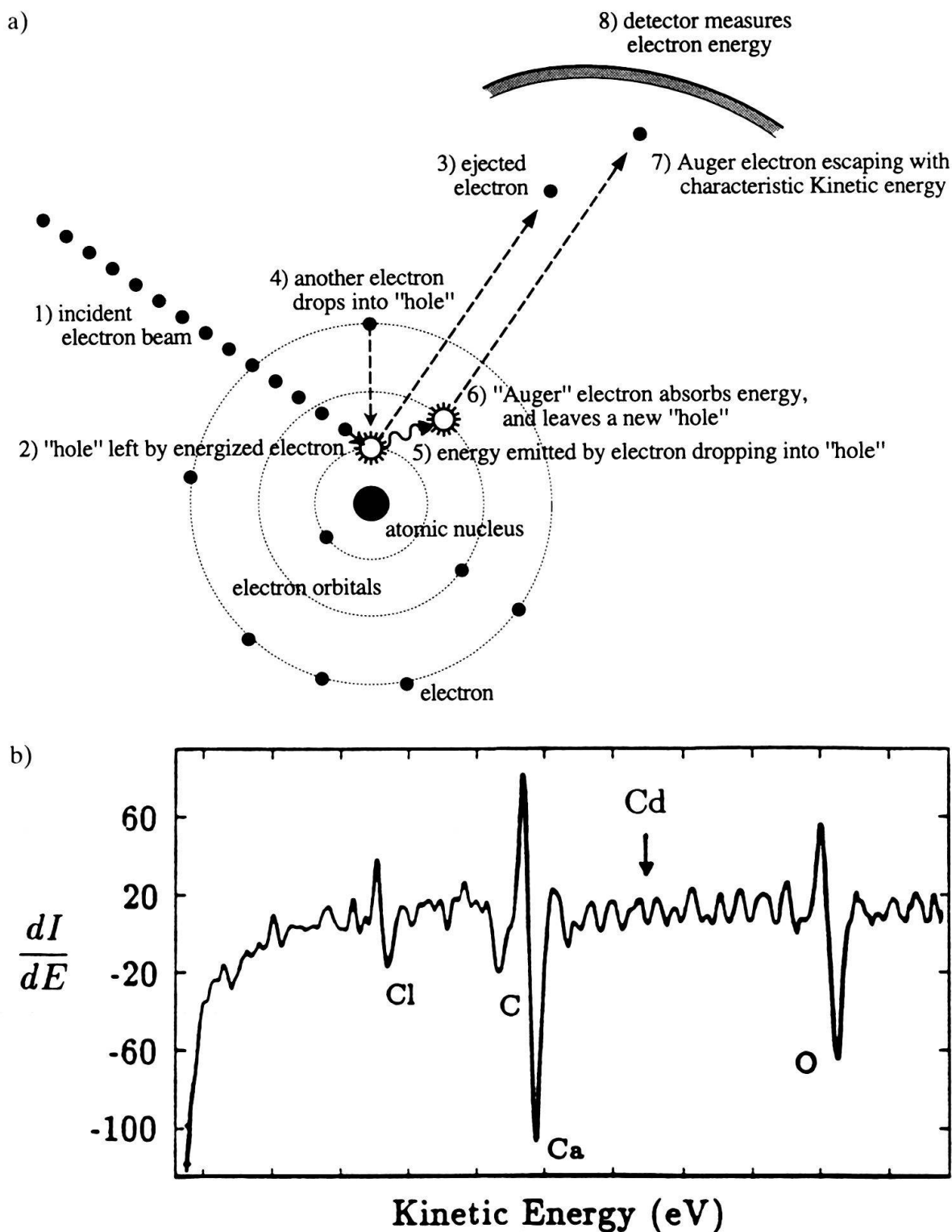


Fig. 2. a) Principles of Auger electron spectroscopy (AES). The numbers refer to steps in the process. The technique requires ultra-high vacuum ($< 10^{-9}$ mbar). Detection limit varies with atomic number and electron configuration. Sensitivity: depth ≈ 10 nm; analysis diameter > 30 nm. Electron beam energy: > 1000 eV. Probes *near-surface*. Details of this technique are available in Hochella (1988) and its references.

b) A typical regional scan of a fresh cleavage face of calcite, fractured in air, exposed to a solution of 10^{-4} M $\text{Cd}(\text{ClO}_4)_2$ in 10^{-3} M HCl for 1 minute, and analyzed two days later. Peaks for the main components of the crystal are present, along with a peak representing surface adsorbed Cl^- ; no Cd can be detected.

Auger electrons are produced whenever electron vacancies are created in a sample, so one can also observe Auger peaks on XPS spectra (Fig. 1a). However, AES usually uses an electron beam as the preferred excitation source. Unlike an x-ray beam, the charged electron beam can be focused to a spot as small as about 30 nm in diameter. This increased lateral resolution is a strong advantage of this technique for two reasons. It is possible to raster the focused beam over the sample to give a scanning electron microscopy (SEM) image of the surface features; then the beam can be focused on a certain chosen location for small spot analyses where chemical identification (all elements except H and He) and relative composition can be determined. Less than a monolayer on the surface can be detected but sensitivity depends on the element's atomic number and electron configuration. In some cases, chemical mapping of surface composition is possible. This technique is useful for geological materials, but care must be taken to minimize artifacts such as surface alteration or preferential desorption caused by the high energy of a focused electron beam. Figure 2b shows an Auger spectrum for calcite that had been exposed to a solution containing Cd^{2+} and Cl^- . Scans are typically presented with the derivative of Intensity with respect to Kinetic energy versus Kinetic Energy.

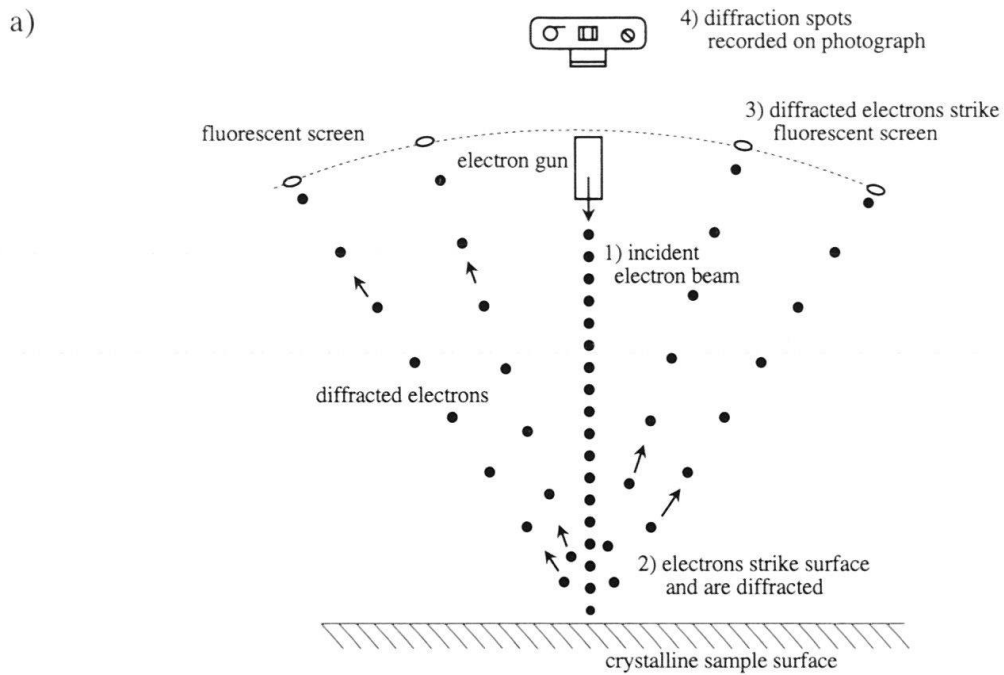
Low-energy electron diffraction (LEED)

With this technique, a diffraction pattern is created using an electron beam with low energy, about 100 eV (Fig. 3a). As with other electron beam techniques, LEED requires ultra-high vacuum. Because the beam has the potential to alter the surface, LEED patterns from carbonates and sulfates must be obtained quickly, within seconds of initial beam impact. Patterns from oxides, silicates and sulfides are typically stable. The depth of analysis is only a few monolayers, or about a nanometer in the case of calcite, making it an ideal technique for probing the atomic structure of a surface, just as traditional x-ray diffraction (XRD) probes the structure of a bulk sample.

An example diffraction pattern for freshly cleaved calcite is shown in Figure 3b. The diffracted electrons strike a fluorescent screen which is then photographed. Some instruments use an electron detector attached directly to a computer. The spacing of the bright spots is a function of the crystal surface unit cell (reciprocal lattice), so their mere presence proves an ordered surface and their spacing identifies the symmetry class and lattice dimensions of the surface. Deviations of this pattern from that expected for the bulk solid gives direct atomic level proof that the surface has somehow been restructured.

Atomic Force Microscopy (AFM)

This relatively new technique uses the attractive and repulsive forces of atoms to create a 3-dimensional image of the surface. Because this microscope is not limited in resolution by the wave-length of light, it is possible to spatially resolve changes in elevation on a scale of tenths or even hundredths of a nanometer. Thus it can be used to examine larger features of surface topography such as cleavage steps, fractures, or crystallites that have grown on the surface, or to observe relative height differences at the molecular scale. It is also useful for studying physical parameters at a local scale and their change with time or



b)

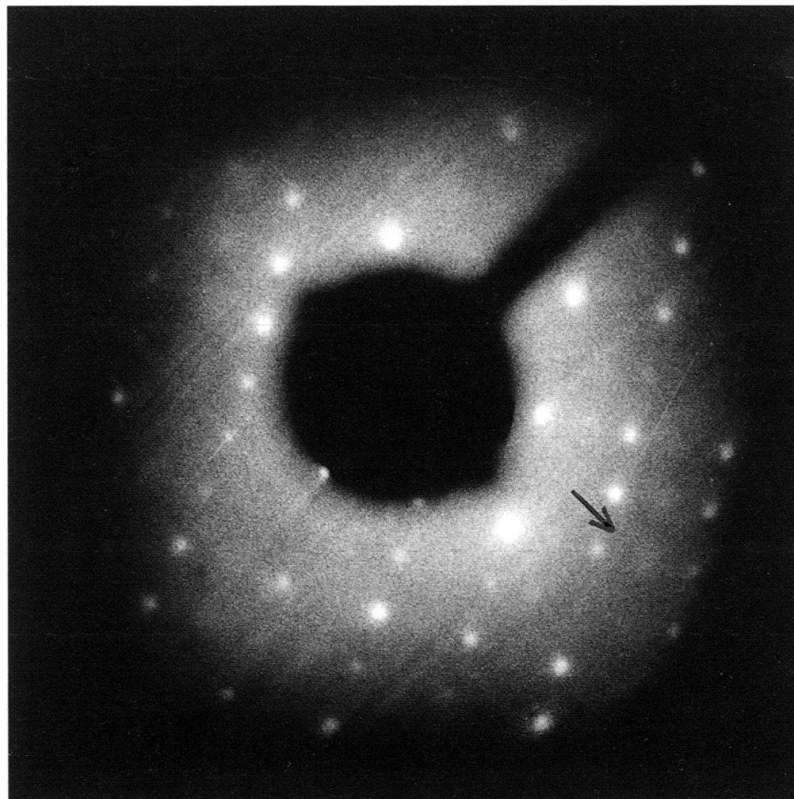


Fig. 3. a) Principles of low-energy electron diffraction (LEED). Numbers refer to steps in the process. The technique requires ultra-high vacuum ($< 10^{-9}$ mbar). Stability of diffraction pattern depends on sample composition. Sensitivity: depth ≈ 1 nm; analysis diameter approximately 1 mm. Probes *near-surface*. Electron beam energy ≈ 100 eV. LEED is well introduced in Clarke (1985). b) A typical diffraction pattern from a sample of calcite, freshly cleaved in air, and introduced into ultra-high vacuum immediately. The spots appear as a reciprocal lattice that is mathematically transformed to give the unit cell. Unit cell dimensions are as expected for the $\{10\bar{1}4\}$ face: $\mathbf{a} = 5.0$ Å and $\mathbf{c} = 8.1$ Å. Weak extra reflections (arrow) indicate doubling of the unit cell in the \mathbf{a} direction, probably as a result of twisting of the surface carbonate groups.

with fluid composition. Such properties as magnetic and frictional forces and “stickiness” (adhesion force) can be investigated.

Mechanically, this technique is not complicated. Figure 4a shows the steps in the process for acquiring a constant force (repulsive mode) AFM image. A sample is held on a piezoelectric element. Upon application of a voltage to specific locations of the piezo scanner, it bends in x or y, or it extends in the z direction by precisely controllable distances. It scans the sample beneath a cantilever holding a pyramidal tip that is as sharp as possible, usually with a radius of several tens of nanometers at its point. A laser, reflected from a mirror, is focused on the back of the cantilever and the position of its reflection is sensed by a photo-diode detector. Change in position of the spot in the detector signals a change in height of the cantilever. The tip is moved toward the sample until they undergo an attractive or repulsive interaction. Images are usually obtained with tracking forces between 10^{-8} and 10^{-11} Newtons. For constant force mode, the spot in the detector (and thus the force) is held constant by a computer feedback loop. A record of the extension of the piezoelectric scanner (Δz) yields a plot in xy representing changes in height. Likewise, scanner height may be held constant while cantilever deflection (force) is recorded. Figure 4b shows a constant force image of the surface of calcite several minutes after cleavage in air.

One of the very important benefits of this technique is its ability to function in ambient conditions. Images of the sample are acquired without the coating or ultra-high vacuum required for SEM imaging. This allows us to study surfaces in air or other atmospheres, and under oil, solvent, water, or solution, during changes in fluid composition, or as time passes. In principal, temperature and pressure can also be controlled. Images at the submicrometer scale allow examination of changes in the topographic surface and images at the nanometer scale allow us to investigate surface atomic structure. It is a technique well adapted to geologic materials because no sample preparation such as thin-sectioning or polishing is necessary.

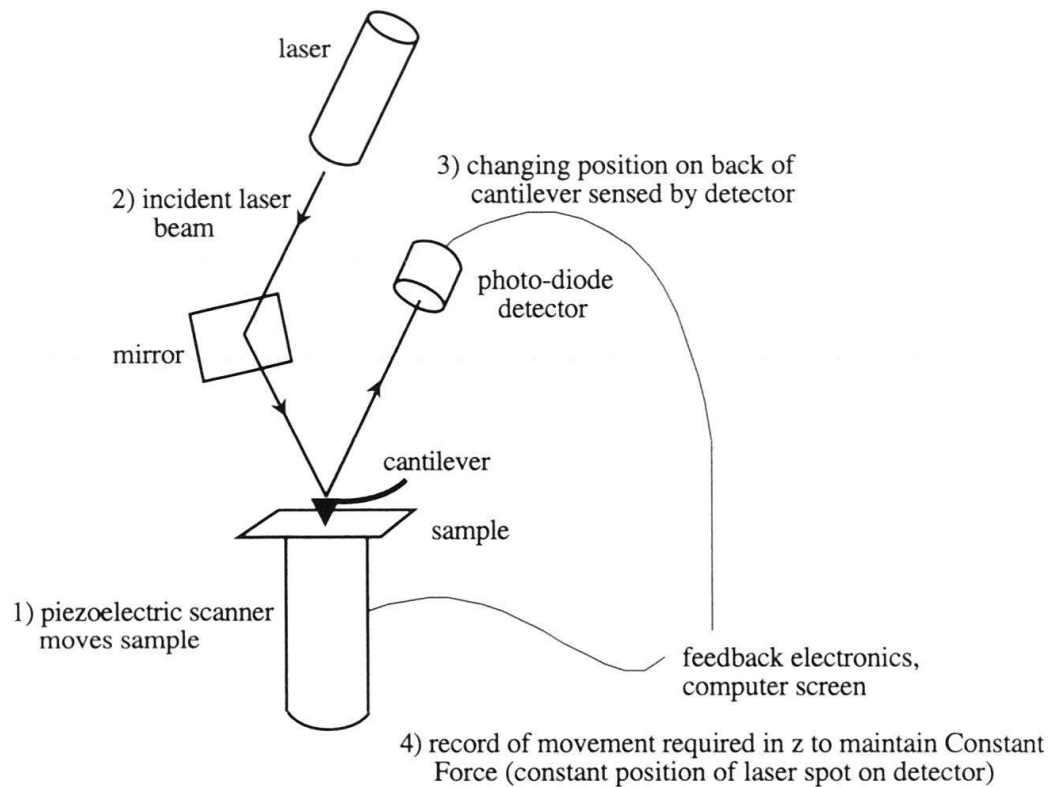
Surface studies of geological materials

Although surface sensitive techniques are not commonly applied to geological materials, there has been work in this direction since the early 1970's. Table 1 lists some of the studies using these techniques on natural samples. More articles can be found in their reference lists. There are also excellent studies using other techniques such as Scanning Tunnelling Microscopy (STM), Secondary Ion Mass Spectroscopy (SIMS), x-ray absorption fine-structure (EXAFS) and many more but for the sake of brevity, these are not listed here.

Surface processes on calcite

In the past, we have learned a great deal about solids from such bulk techniques as x-ray fluorescence (XRF), transmission electron microscopy (TEM), electron probe microanalysis (microprobe or EPMA) and x-ray diffraction (XRD), and about solutions from traditional wet-chemistry techniques such as solution composition, pH, pe and conductivity. We have some understanding of mineral-fluid interactions elucidated from years of study using petrology and thermodynamics. Our hydrogeochemical models are based on

a)



b)

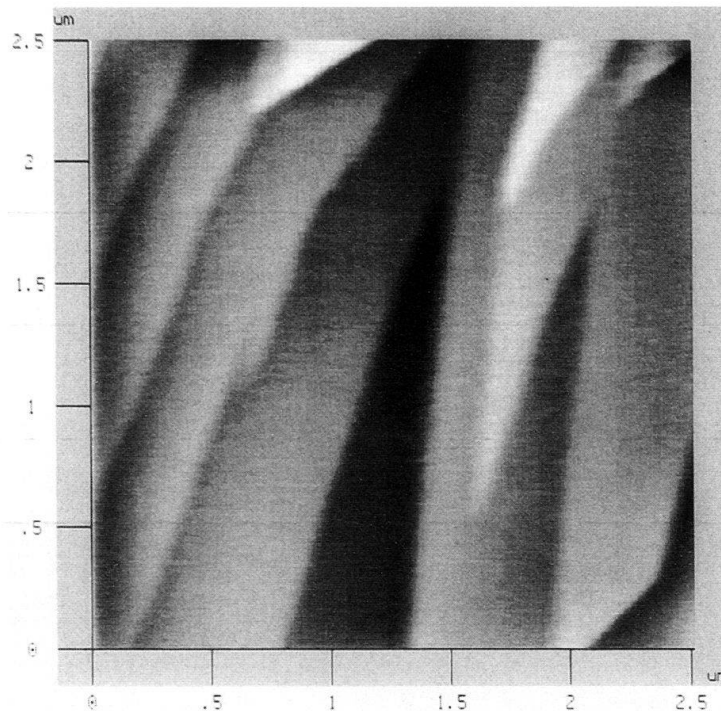


Fig. 4. a) Principles of atomic force microscopy (AFM). Explanations on the diagram are for constant force mode. Experiments may be carried out *in situ* in air, in solution or under controlled atmosphere. Sensitivity: vertical $< 0.1 \text{ \AA}$; horizontal $\sim 2 \text{ \AA}$. Force of tip on sample usually set between 10^{-8} and 10^{-11} N . *Surface* features only. One can learn more about AFM and its applications in Rugar & Hansma 1990, Descouts & Siegenthaler 1992 and Güntherodt et al. 1994. b) A typical constant force mode image of the cleavage face of calcite, freshly cleaved immediately before imaging in air. The scan took ten minutes to complete. White parts of the image are closest to the viewer; grey is further away, and black is furthest. Terraces are 1 monolayer or 3 \AA high.

Mineral Group	Study of:	Techniques	Reference
Oxides MnO ₂ Hematite	metal adsorption surface and atomic structure	XPS AFM	Brulé et al., 1980 Johnsson et al., 1991
Sulfides Pyrrhotite Pyrite	oxidation adsorption of Au	XPS XPS	Buckley & Woods, 1985a, b Hyland & Bancroft, 1989
Silicates Feldspar Clays Labradorite Quartz, albite, jadeite, nepheline, diopside, olivine Diopside Albite Albite	dissolution metal adsorption dissolution structure and composition composition atomic structure dissolution	XPS XPS AES XPS XPS AFM, LEED XPS, AFM	Holdren & Berner, 1979 Dillard et al., 1981 Hochella et al., 1988 Hochella & Brown, 1988 Eggleston et al., 1989 Hochella et al., 1990 Hellman et al., 1990 and Drake & Hellmann, 1991
Illite/smectite	microstructure	AFM	Lindgreen et al., 1991
Carbonaceous Matter	crack surfaces	XPS	Tingle & Hochella, 1993
Carbonates Calcite Calcite, magnesite, Mg calcite, and dolomite Calcite, Calcite Aragonite Calcite Calcite	adsorption of Ba, Pb adsorption of Mg uptake of Pb uptake of Zn uptake of Sr uptake of PO ₄ dissolution and precipitation	XPS AES XPS XPS XPS AFM AFM	Bancroft et al., 1977a, b; 1979 Mucci & Morse, 1985; and Mucci et al., 1985 Fulghum et al., 1988 Zachara et al., 1989 Plummer et al., 1992 Dove & Hochella, 1993 Hillner et al, 1992 and Gratz et al., 1993
Calcite Calcite	atomic structure surface reactions and structure, uptake of Cd, Zn.	AFM XPS, LEED, AES, AFM	Ohnesorge & Binnig, 1993 Stipp & Hochella, 1991; Stipp et al., 1992; 1994

Tab. 1. Partial list of studies using XPS, AES, LEED or AFM to investigate geological materials.

this information. However, studies at a macroscopic level often provide an averaged picture, with the risk of making several individual processes appear as one. With techniques that allow us to study surfaces, and that give us direct, molecular-level information, we can test theories that have already been developed from macroscopic data, and we can extend our knowledge of the mechanisms that take part in processes at the interface.

In the next paragraphs, examples of the use of XPS, AES, LEED and AFM will be presented. More extensive details of these studies can be found in Stipp & Hochella 1991, Stipp et al. 1992, 1994, Stipp and Eggleston 1994. Here, the purpose is twofold: to show how, using surface techniques, the theory of a hydration layer on a calcite surface has been tested, and then, to show how the currently understood process of trace metal up-

take involves not only adsorption and coprecipitation, but also, in the case of calcite, the solid-state diffusion of Cd^{2+} and Zn^{2+} into the calcite surface.

Hydration

Adsorption theory (Parks 1975; Stumm & Morgan 1981), based on years of solution chemistry work, proposes that charged mineral surfaces are satisfied by oriented and/or hydrolysed water molecules. Thus the surface can be thought of as a pattern of $\text{S}\cdot\text{OH}^-$ and $\text{S}\cdot\text{H}^+$ surface species (where $\text{S}\cdot$ represents a charged site on the mineral surface). Molecular level proof that this is so comes from XPS and LEED data collected from a pristine surface of calcite and from a similar surface exposed to water as liquid or as vapour. Figure 5 shows carbon and oxygen XPS scans for these two samples. Although we cannot analyze for H directly, we can see its effect on bonding environments. On the carbon peak for the sample exposed to water (Fig. 5b), the slightly higher binding energy shoulders represent atoms that find themselves in environments where the C–O bonds are stronger than in a typical CO_3 group; HCO_3 has such an environment. On the oxygen peak from the water exposed sample, the shoulder represents atoms in a Ca–O–H environment whereas the main peak represents the Ca–O–C bonds found in bulk calcite and similar to those on a surface prepared in ultra-high vacuum in the absence of water vapour. The sample that had been exposed to water as vapour or as liquid retains evidence of surface hydration species $\text{S}\cdot\text{CaOH}$ and $\text{S}\cdot\text{CO}_3\text{H}$ even when the sample is dried and stored under ultra-high vacuum for several weeks. The small relative peak intensity of the shoulders corresponds to the small contribution of species on the actual surface relative to that within a sampling volume having a depth of about 30 monolayers. Samples exposed to solutions for long periods, where precipitation or dissolution had been taking place before exposure to ultra-high vacuum show even larger shoulders representing surface species (Stipp and Hochella 1991).

Comparison of peak intensity ratios (Tab. 2) gives independent confirmation for the presence of hydration species. Although we cannot measure relative H increase, there is

Sample History	O/C	O/Ca	Ca/C
Cleaved in ultrahigh vacuum (as "clean" as possible)	3.0	3.0	1.0
Cleaved in air (humidity present)	4.5	4.5	1.0

Tab. 2. Ratios of XPS peak intensity for the components of calcite. Peak intensity is determined from the area under the peaks and normalized, assuming that the "clean" (in-vacuum fractured) sample is stoichiometric. The sample exposed to air with its ambient humidity shows an increase of oxygen with respect to the other components.

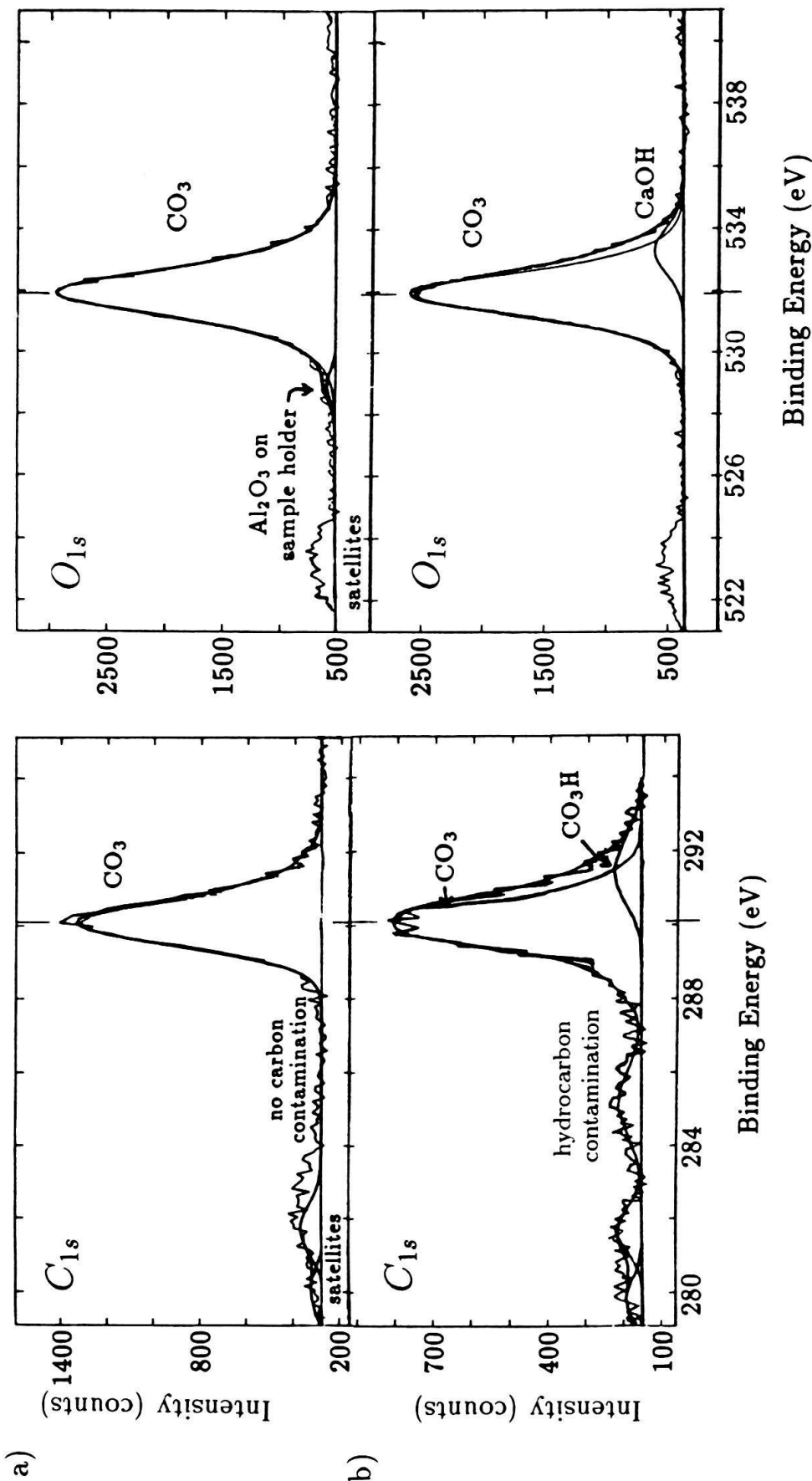


Fig. 5. XPS spectra from a calcite surface for C_{1s} and O_{1s} (photoelectrons originated in the 1S orbitals). Absolute binding energies determined through referencing to gold.

a) Sample analyzed soon after cleavage in ultra-high vacuum. Left is the carbon spectrum; there is no adventitious carbon contamination on the surface. The main peak represents carbon in CO_3 bonds. The oxygen spectrum, on the right, shows a peak with the typical Ca-O-C environment for calcite.

b) Sample cleaved in air with exposure to ambient humidity, introduced to ultra-high vacuum and analyzed immediately. Some carbon contamination is present and a higher binding energy shoulder representing CO_3H has appeared on the main carbon peak. On the oxygen spectra, a shoulder representing the presence of one or more new environments for O.

a strong increase in surface O with respect to both Ca and C on the water exposed sample as compared to the pristine surface. Samples with extended exposure to solutions at equilibrium with the atmosphere also show an increase in the surface concentration of CO_3 with respect to Ca.

The LEED pattern from a surface of calcite freshly cleaved in air (Fig. 3b) shows an ordered surface, with lattice parameters as expected for bulk calcite. However, there are very weak extra reflections (arrow) that represent a doubling of the unit cell in the **a** direction. AFM images taken in air and under distilled water that has equilibrated with the calcite surface confirm this 2×1 lattice pattern (Stipp et al. 1994). The observed restructuring probably results from surface carbonate groups that are twisted with respect to their crystallographic orientation in the bulk and certainly results from stabilization of dangling bonds produced during cleavage, most likely by the hydration species observed using XPS.

XPS, LEED and AFM collectively give supporting evidence that the surface of calcite is hydrated, and that the presence of surface species alters the atomic structure and bonding environments at the surface from that expected on a simple termination of the bulk calcite structure. This helps to confirm the theory of surface hydration, and it also extends our understanding of the behaviour of the hydration layer in dry environments. If we see hydration species on samples exposed only to air, and preserved after days of exposure to ultra-high vacuum, then it is clear that these hydration species are tightly bonded to the surface. Our mechanistic models for carbonates must consider reactions with hydrated surface species rather than simply considering the bulk stoichiometric solids if we hope to form a correct molecular understanding of chemical reactions in natural systems. These systems include humid geological environments but in addition, such "dry" environments as unsaturated soil and air.

Solid-State Diffusion

Wet chemistry studies of divalent metal uptake by calcite (McBride 1979, 1980, Lorens 1981, Zachara et al. 1991 and many others) show a two stage process where "fast" uptake is followed by "slow". The first stage is interpreted to be adsorption whereas the second stage is generally thought to result from coprecipitation or in one model, from dehydration of an amorphous layer (Davis et al. 1987).

XPS results demonstrate that cadmium and zinc are certainly adsorbed on calcite from undersaturated solutions but surface concentration after removal from solution is observed to decrease with time (Fig. 6a and b). Experiments with radiolabelled ^{109}Cd , a γ -emitter that can be detected in the solid phase, prove that the Cd is still present in the sample and that it is not evaporated off in the vacuum chamber nor is it selectively desorbed by the x-ray beam.

Samples where epitaxial layers (confirmed by LEED and XPS) of CdCO_3 had been grown over a fresh cleavage surface of calcite show a loss of Cd^{2+} in the top few nanometers with a parallel gain of Ca as time passes (Tab. 3). This process occurs in air and in ultra-high vacuum where solution aided recrystallization cannot occur. The XPS peaks for C, Cd and O show a progressive shift of binding energy as the composition of the surface changes from 0 to 100% CaCO_3 , suggesting the development of solid-solution by

solid-state diffusion (Stipp et al. 1992). Similar experiments with Zn^{2+} adsorbed on calcite show a parallel loss of trace metal in the surface with time (Fig. 7). These studies indicate that Cd and Zn move away from the surface into the bulk at a rate of nanometers in days to weeks. This illustrates the contribution of solid-state diffusion in the overall process of Cd and Zn uptake and suggests that it may also play a part in the uptake of other divalent metals.

In order to verify that the metal did not diffuse along the surface and then into cracks, the surface was examined with AES and AFM. With AES in raster mode, a SEM image was made several hours after a sample had been exposed to an undersaturated solution of trace metal. The calcite surface appears to be flat at the μm scale; cleavage steps and scratches made intentionally on the face are observable, but there are no visible cracks to

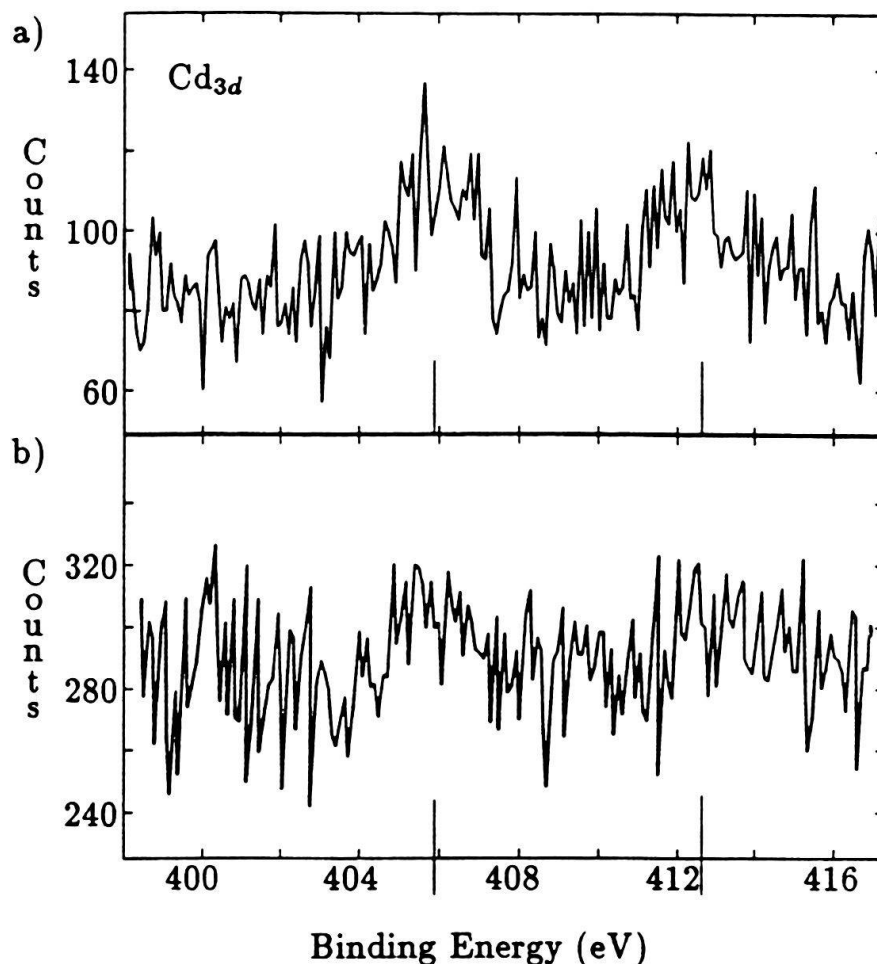


Fig. 6. XPS spectra of the region where Cd_{3d} peaks are expected for two samples of calcite exposed to solutions of 10^{-4} M Cd (undersaturated). Surface charging effects corrected for by referencing to gold.

a) Exposure for one minute results in uptake equivalent to a monolayer (measured by radiotracer $^{109}Cd^{2+}$). The sample was analyzed immediately; the two peaks expected are weak, but above background.

b) Exposure for 100 minutes results in uptake of four equivalent monolayers. The sample was analyzed two days later. Although we would expect four times the intensity, the expected Cd peaks are not above background. γ -counting proved the Cd remained in the sample, but it was no longer in the near-surface (< 10 nm).

Sample History	Cd/Ca	Intensity of Ca peak	Analysis depth (approx.)
2 months exposure to solution analyzed immediately after drying	65	barely above background	90 Å
2 months exposure to solution analyzed after 1 month in vacuum	2.8	very clear	30 Å

Tab. 3. Cd²⁺ adsorption and disappearance into calcite. Relative peak intensities show a loss of Cd and a gain of Ca in the surficial zone with time. The initial solution had been saturated with CdCO₃ and pure CO₂ with no Ca. Slow degassing during two months caused precipitation of a CdCO₃ overlayer on the calcite template. Immediately after removal from solution, the overlayer is essentially pure CdCO₃ with chemical composition (XPS) and structure (LEED) identical with otavite (CdCO₃). After a month in the dry environment of the ultra-high vacuum chamber, we see a development of Cd_{1-x}Ca_xCO₃ which has bonding strengths between those of both pure calcite and pure otavite.

serve as conduits for surface migration of adsorbed metals. Using the small spot analytical capabilities, each “defect” type was examined to search for anomalous concentrations of Cd. No Cd is found anywhere except on one location on one sample; a small peak occurs at a scratch that had been inscribed with a scalpel. Thus, Cd disappears from the whole surface on the unscratched samples, without a trace of its pathway.

AFM images taken in air of a freshly cleaved calcite surface show flat cleavage planes with monolayer steps (Fig. 4b); no fractures are apparent even on a scale of nm. Imaging of the same area after several hours in air (Fig. 8a and b) shows that spots have formed on the surface. After a week (Fig. 8c), the surface is completely recrystallized. Clearly, if divalent metal had been adsorbed, it could be moved and/or incorporated into the dynamic surface.

Thus, XPS, AES, LEED and AFM have given complementary information about the processes involved in the uptake of divalent metals by calcite. Although adsorption and incorporation by reprecipitation and coprecipitation in solution are important processes, surface and solid-state diffusion are also important in surface mixing and incorporation. By taking advantage of the dry, ultra-high vacuum conditions, it has been shown that incorporation of adsorbed species also occurs in the absence of water. This has special implications in arid regions and in ecosystems where groundwater levels vary seasonally. If our hydrogeochemical models fail to recognize the processes of surface and solid-state diffusion, they will inevitably give inaccurate predictions of trace element uptake in carbonate terrains. The total proportion of Cd, Zn and possibly other divalent metals that is potentially removed from or released to ground or surface waters may be underestimated if it is assumed that uptake by adsorption ends when the surface becomes saturated.

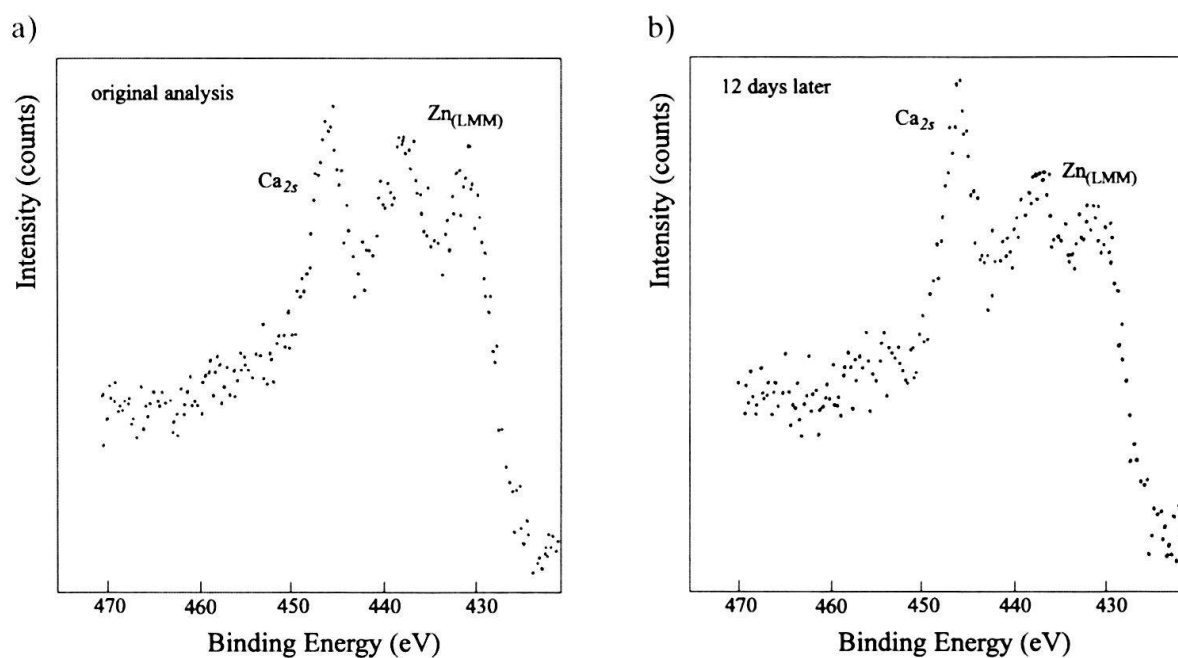


Fig. 7. XPS spectra of a sample of calcite exposed to a supersaturated ZnCO_3 solution for several days. a) Original analysis shows the presence of both Ca (XPS) and Zn (AES) peaks. b) Analysis of the *same* sample 12 days later shows a decrease in Zn intensity with a subsequent increase of Ca. The sample had been stored in a covered container, in dry air, showing that incorporation has taken place in the absence of a solution phase.

Conclusions and Summary

In order to be effective, hydrogeochemical models must be based on sound understanding of the molecular processes that take place at the interface of solid with fluids. In earth sciences, we could learn much more about these fundamental processes by taking advantage of existing surface-sensitive techniques that allow us access to direct, molecular-level information about changes in chemical bonding, lattice structure and surface topography during reactions involving natural materials. In particular, XPS, AES, LEED and AFM have been used to gain fundamental understanding of some chemical processes that take place at the calcite surface. They have shown that calcite is covered with a hydrated layer over an ordered surface when in contact with solution, or even in very dry conditions, and that adsorbed Cd and Zn move away from the surface into the solid to form a solid-solution spontaneously.

In general, these techniques offer a means to examine all sorts of natural surfaces in fundamental or applied studies. XPS and AES provide chemical information *about the top 10 nm of a surface*. XPS is particularly useful for information about chemical bonding and AES can provide chemical maps of a surface with resolution on the scale of about $0.1 \mu\text{m}$. Fractions of a monolayer of adsorbed material can be detected using either of these techniques but sensitivity falls off sharply when the element is located inside the sample. H and He are undetectable; sensitivity to the other elements is a function of atomic number and electronic configuration. Adventitious carbon contamination on the surface can selectively hamper electron escape and thus alter relative element intensities

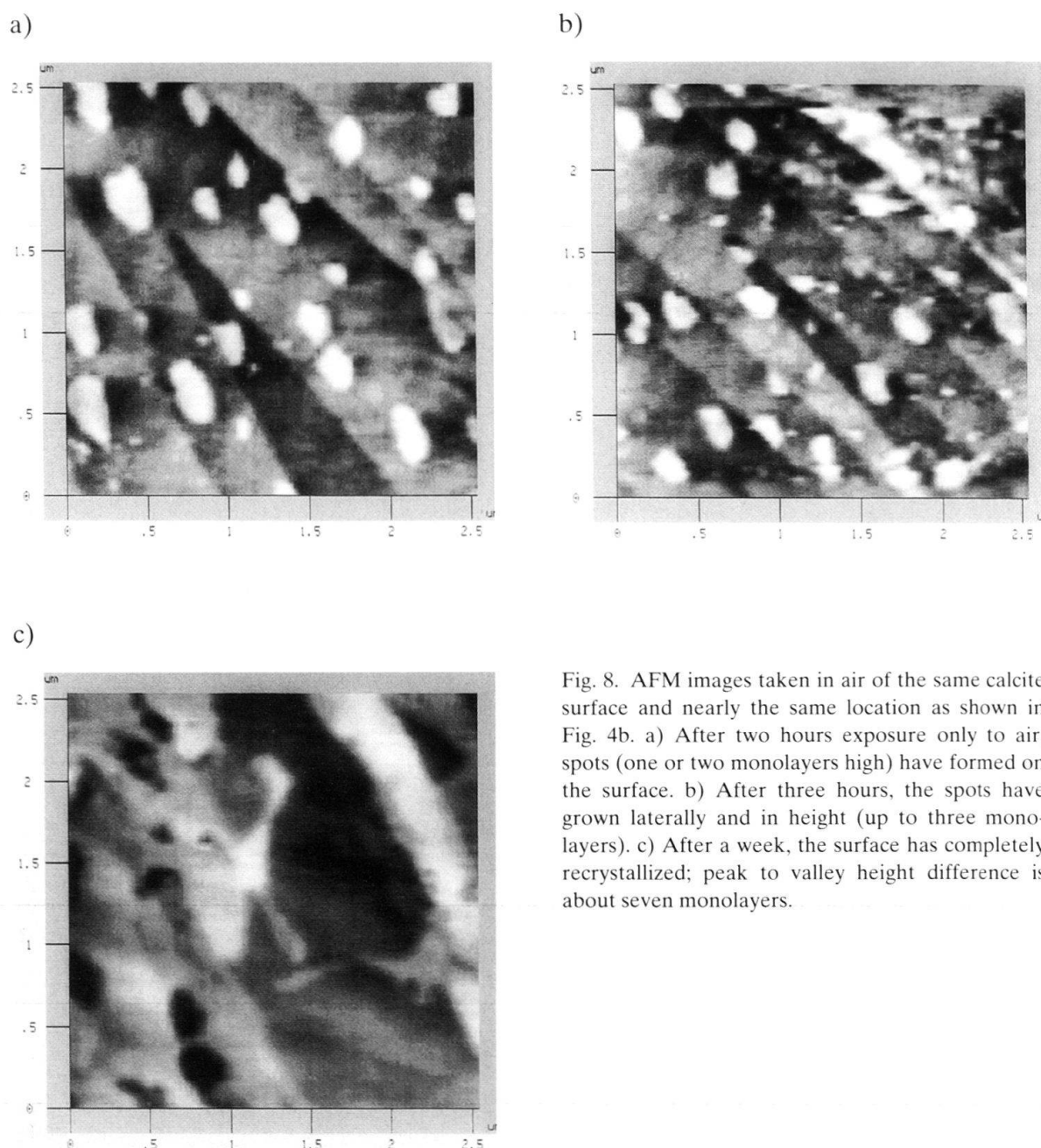


Fig. 8. AFM images taken in air of the same calcite surface and nearly the same location as shown in Fig. 4b. a) After two hours exposure only to air, spots (one or two monolayers high) have formed on the surface. b) After three hours, the spots have grown laterally and in height (up to three monolayers). c) After a week, the surface has completely recrystallized; peak to valley height difference is about seven monolayers.

but samples can be cleaned to reduce this problem. Both single crystals and powdered material can be analyzed. The requirement of ultra-high vacuum makes *in situ* studies impossible and introduces artifacts because of drying, but important information about sample history can be obtained.

LEED provides information about the atomic structure *for the top few monolayers of a surface*. It also requires ultra-high vacuum so direct dynamic studies are impossible, but it likewise can provide important information about a sample's history. Only single crystals of several millimeters diameter can be analyzed, and because of the high surface sensitivity, the contamination layer must be minimal (< 2 or 3\AA).

AFM gives physical information on a local scale (several nm laterally) *from only the surface*. Often this information is topographic (repulsive force) but we can also observe lateral changes in magnetic, friction and attractive forces. Atomic structural information can also be obtained. Because ultra-high vacuum is not necessary, *in situ* studies with changing conditions are favoured. Single crystals or particles with diameter less than a micrometer can be examined if a means to stick them to a surface can be found. The ability to examine *only the surface* means that the surface contamination layer will be observed. This layer can be scraped off using the AFM tip during imaging or it can be removed chemically, prior to imaging. AFM at present is generally unable to give chemical information. However, in carefully controlled conditions, changes in a physical parameter on a surface can be correlated with exposure to a specific chemical component.

Singly or together, these surface sensitive techniques can complement information gained from traditional wet-chemical methods and/or bulk analytical techniques. They can contribute to a better understanding of conditions at a local scale that has not been directly possible using a macroscopic approach.

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