detoxification mechanisms or defenses against predators), or both, is not yet fully established.

This latitudinal trend of greater diversity, more numerous plant defenses, and increased herbivore pressure in the tropics suggests that climate is important. Wilf and Labandeira tested this hypothesis by examining floras from the late Paleocene (~56 million years ago) and the early Eocene (~53 million years ago). During this 3-million-year interval, temperatures in their study area warmed by about 7°C, changing the climate from humid temperate to humid subtropical. Consistent with the latitudinal data, they found that plant diversity increased, the amount of herbivore damage to leaves increased, and the diversity of herbivores per plant species increased. In addition, more abundant species suffered higher damage rates, again consistent with data from modern communities (*10*).

A Lepidopteran caterpillar with warning eyespots.

It is perhaps tempting to extrapolate from these patterns to predict changes in plant-animal interactions caused by the current global warming trend. Such extrapolations may be misguided, however, because the rates of climate change today are several orders of magnitude faster than before. This rapidity may not permit significant evolutionary change or plant dispersal, and is more likely to disrupt existing plant-herbivore associations (*11*).

Although Wilf and Labandeira's study may not be able to directly predict future changes in plant-herbivore interactions, it goes a long way toward explaining present and past communities. These data are exciting because they suggest that the greater capacity for plant-herbivore interactions in tropical as compared to temperate climates may have been the case throughout the last 100 million years in which angiosperms (flowering plants) have been diverse. Thus, climate may lead to different evolutionary histories, with herbivores and plants exerting stronger selective pressure on each other in Earth's warmer zones. Climate may also influence the dynamics of herbivore and plant populations, with herbivores being more abundant, more diverse, and more damaging in tropical climates. Their work also suggests that fossil evidence can be used productively to test ecological theories, and this should encourage more dialogue between neo- and paleoecologists.

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PERSPECTIVES: MAGNETISM

Shining Soft X-rays on Magnetic Structures

Ulrich Hillebrecht

The study of magnetic materials with x-rays is developing at a breathtaking pace. The methods used in these studies extend magneto-optics—the response of a material to optical excitation as a function of the relative orientation of magnetization and light polarization—to the x-ray regime. One of the key advantages of these techniques is that they are element specific, because the photon wavelength (or energy) in the x-ray regime can be tuned to match the excitation energy of a discrete core electronic level. Also, layer thicknesses of magnetic multilayers and lateral structures in novel magnetic devices that are presently being developed are comparable to soft x-ray wavelengths. Therefore, detailed insight into the magnetic properties of these technologically important magnetic structures can be obtained by use of soft x-rays. The soft x-ray regime is of importance because all technically relevant magnetic materials contain 3d transition metals, for which the 2p excitation that shows the highest sensitivity to the magnetic state lies between 500 and 1000 eV.

Synchrotron radiation is a particularly powerful tool for soft x-ray magneto-optics, offering tunability to virtually any core level resonance, high intensity and brilliance, good collimation, and complete control over polarization. Recently developed polarizers and wave retarders allow us to analyze and modify the state of polarization for soft x-rays (*1*), further increasing the scope of these magneto-optic studies. On page 2166 of this issue, Dürr *et al.* (*2*) demonstrate the power of x-ray magneto-optics in a synchroton study of single crystalline FePd layers, which provides detailed insights into their complex magnetic domain structure.

In a classical picture, magneto-optic effects occur when the magnetic field associated with a magnetic material acts on the electron currents induced by an incident electromagnetic wave. A charge moving in a magnetic field experiences the so-called Lorentz force, the direction of which is normal to the velocity of the charge and the magnetic field (see top figure on page 2100). The Lorentz force leads to light with polarization perpendicular to the incident light in the reflected beam. Microscopic theories (*3*) show that this magneto-optic effect is connected to excitations from the core shell to spin-polarized unoccupied electronic states and the interaction of magnetic moments due to the spin of the electrons and their orbital motion.

The change of polarization when light is passed through a magnetic material, known as the Faraday effect, is in principle

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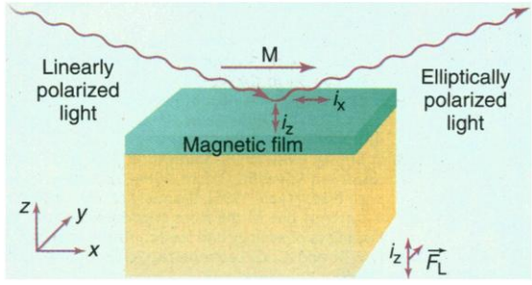


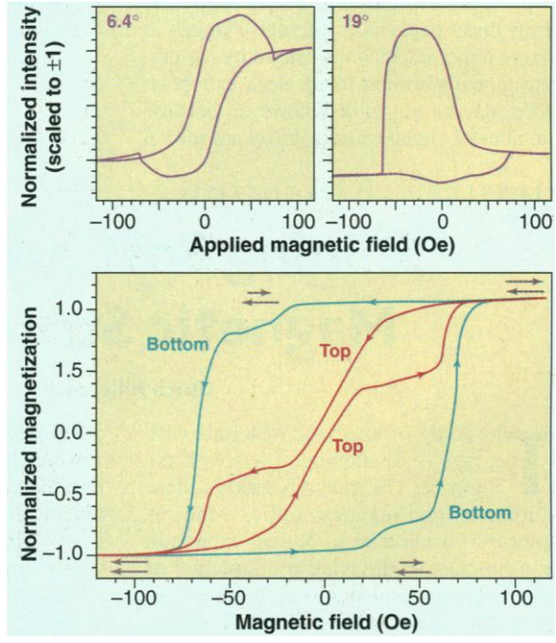
Phenomenological model of the magneto-optic response. An incident linearly polarized wave generates an oscillating current I in the plane of incidence with components i_z and i_x along the x and z directions. For magnetization M along the x direction, the current along z experiences a Lorentz force along y. This gives rise to polarization perpendicular to the incident beam; the normal reflected beam was omitted for clarity. In the soft x-ray regime, this effect can be detected as a change of the polarization on reflection or a change in the magnitude of the reflected intensity.

the most direct way to measure the optical constants responsible for magneto-optics (*1*). The late Theo Thole, Paolo Carra, and co-workers at the European Synchrotron Radiation Facility in Grenoble, France, showed how one can determine local magnetic moments, distinguishing between different constituents and spin and orbital parts, from magneto-optic spectroscopy in the core level regime (*4*). Also, the study of magnetic properties by scattering experiments, both with hard (*5*) and soft (*2, 6, 7*) x-rays is increasing rapidly. In a scattering experiment, one measures the number of outgoing photons as a function of direction, or transferred wave vector, thus probing the spatial arrangement of scattering centers. The wavelength of the photons to be scattered then has to be comparable to the distances between atoms. Another property of central importance for scattering experiments is the coherence of the incident light: For interference to take place between waves emerging from different atoms, the light incident on these atoms has to have a fixed phase relationship.

Research on magnetic materials is currently focused on layered samples of increasing complexity, containing magnetic and nonmagnetic layers configured so as to provide the best performance for a particular application. Surface and interface roughness play an important role in the magnetic properties. Freeland *et al.* (*7*) showed in diffusely scattered light measurements that the magnetic moment distribution appears to be smoother than the chemical interface. A multilayer reflects and transmits light at every interface, and the interference between these waves gives rise to a periodic modulation of the overall reflected and transmitted intensity. This allows one to determine geometry and interface properties of the multilayer. For regular assemblies of magnetic units—multilayer films (*6*) or regular domain patterns (*2*)—the magneto-optic signal shows similar modulations, which reveal information about the magnetic structure.

Magneto-optical scattering was used recently in a beautiful experiment on a magnetic sandwich consisting of two Co layers separated by a Cr layer a few nanometers in thickness (*6*). The Cr layer mediates an exchange coupling between the two ferromagnetic Co layers, such that their magnetizations are not completely independent. Monitoring the reflected intensity at the Co 2p excitation energy as a function of applied field yields the ferromagnetic hysteresis loop. Using visible light, one would just see the overall magnetization, because the wavelength and probing depth would be large compared with the film thickness. In contrast, measurements with x-rays with wavelengths comparable to the film thickness reveal modulations of the reflected intensity as a function of incidence angle, typical for layered structures. In addition, the hysteresis loops change qualitatively with incidence angle. In principle, the loops should show inversion symmetry, but as can be seen in the figure to the right, for certain incidence angles, this is not the case. The asymmetric shape results from the interference of the magneto-optic response from the two layers, which are not equivalent because of the differing sequence of interfaces: The bottom film is sandwiched between a semiconductor substrate and Cr, whereas the top film is between Cr and an Al cap layer. Taking this into account, one obtains symmetric loops for each layer. However, these loops are not identical (see figure at right), contrary to naïve expectation for films of the same material, thickness, and crystal structure. This shows that anisotropies and magnetic switching are influenced by the layer sequence and provides information about the coupling strength and magnetic correlation function between the two layers, all of which are important aspects for the development of novel magnetic devices based on interlayer exchange coupling.

The report by Dürr *et al.* (*2*) in this issue uses a similar approach to characterize the lateral magnetic structure in a chemically homogenous thin film. In a thin film with perpendicular magnetic anisotropy, the shape of the film may cause a competing shape anisotropy, leading to a domain pattern with some regularity. The typical length scale for this domain structure is on the order of a few tens of nanometers, and the resulting best suited wavelength for scattering is close to the 2p excitation threshold of Fe, where a large magneto-optic response can be exploited. Magnetic scattering occurs because scatterers are magnetically inequivalent, as in an antiferromagnet. Dürr *et al.* transfer this idea to oppositely magnetized domains, which by way of self-organization form a regular array. The experiment shows the presence and size of closure domains that are not visible by magnetic force microscopy or other methods. These closure domains stabilize the magnetic



An asymmetric response. Magnetic hysteresis loops measured for a Co/Cr/Co trilayer at different incidence angles θ [adapted from (*6*)], with circularly polarized radiation tuned to the Co 2p excitation. A trilayer consisted of 5 nm of Co, 3.5 nm of Cr, and 5 nm of Co, grown on a semiconductor substrate. The reflected intensity was measured as a function of magnetic field applied along intersection of sample surface and plane of incidence, which coincides with the axis of easy magnetization. For some incidence angles, symmetric hysteresis loops are observed (**top left**), whereas extremely asymmetric loops appear at other angles (**top right**). From a collection of such curves, the hysteresis loops for the top and bottom Co films can be deduced separately.

structure and control the speed of magnetization reversal, which is a key issue in device applications.

The importance and the scientific attraction of the type of investigation described here are reflected in the broad activities at numerous synchrotron radiation sources. Novel magnetic devices such as magnetoresistive and spin-polarized tunneling read heads or nonvolatile memories depend on controlling the properties of ever smaller magnetic structures, to which the new analytical methods that use soft x-rays will provide a substantial input.

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PERSPECTIVES: GEOCHEMISTRY

Nature's Gold Factory

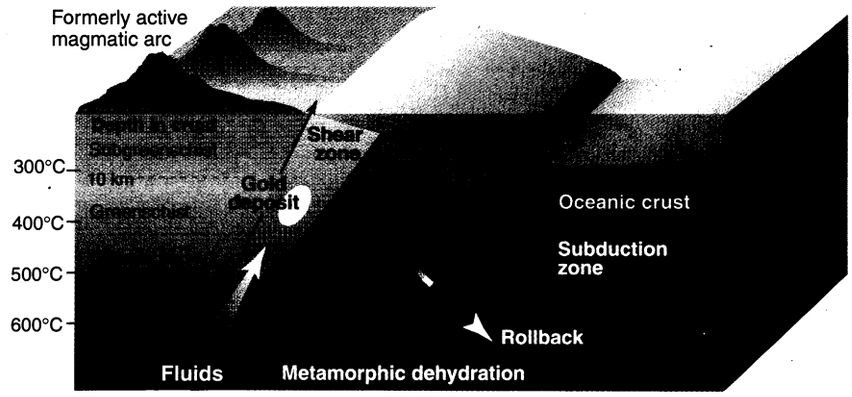
Robert Kerrich

Gold is one of the least reactive, or most noble, metals and at 2 parts per billion in weight is also one of the rarest elements in Earth's crust. Yet hot waters circulating deep in the crust may leach gold from large volumes of rock and precipitate it at about 400° to 300°C in vein deposits, where it is concentrated at up to 10,000 times the background level. These observations have elicited a number of questions that are the subject of contentious debate (*1*): (i) Which aqueous species dissolves the "unreactive" gold; (ii) why is gold concentrated in the vein deposits whereas metals such as Pb, Zn, and Cu that are 1000 to 100,000 times more plentiful in crustal rocks are not; (iii) under which hydrothermal conditions is the aqueous gold species soluble (*1*); and (iv) why do the majority of gold deposits form over such a narrow temperature window of about 400° to 300°C, in greenschist metamorphic environments (*1*) (see the figure)? On page 2159 of this issue, Loucks and Mavrogenes report a set of elegant experiments that can answer all these questions thus explaining empirical observations of vein gold deposits (*2*).

Gold is a rare metal in Earth's crust for three principal reasons: astrophysical, atomic, and terrestrial. Main-sequence stars like the sun burn first H and He and then heavier elements, up to ^{56}Fe, in fusion reactions. Elements heavier than ^{56}Fe can only be born by neutron capture reactions in rare astrophysical events termed supernovae, and therefore gold is inherently rare. In addition, all nuclides with odd atomic numbers are rare compared with even numbered neighbors because their nuclei are less stable, resulting in ^{79}Au being even less abundant than ^{78}Pt and ^{80}Hg. Finally, as the terrestrial planets accreted, liquid iron settled gravitationally through the liquid silicate shell to form Earth's iron core, taking gold and other siderophile (Fe-loving) elements such as Pt, Pd, Ir, and Rn with it. Much of Earth's gold inventory is thus sequestered in its core, further reducing its abundance in the crust.

Exceptionally extensive natural processes are therefore required to concentrate this rare, unreactive metal from crustal background levels into rich vein gold deposits. Consider an example of such a natural chemical factory. Four thousand tonnes of gold have been mined from the 300 km by 200 km Abitibi greenstone belt, part of the 2.7-billion-year-old Canadian Shield. Gold is only mined from veins with economic grades, so the actual amount of gold concentrated in this belt may be 10 times greater. If leaching efficiency in the source rock is 50%, then the source volume would have to be 20,000 km^3, equivalent to a block of crust about 50 km by 50 km and 8 km deep. An estimated 1000 km^3 of aqueous fluids with a starting temperature of 500°C must have leached this block of crust, transported gold as an aqueous species, and become channeled along faults where gold precipitated with quartz in vein deposits over the "magic" temperature interval of 400° to 300°C (see the figure).

What is the underlying solution chemistry that may enable this geochemical feat? Although gold is relatively unreactive and gold compounds are generally not very stable, gold has been shown to dissolve in aqueous fluids by forming Au-Cl or Au-S complexes (*1*). Au-carbonyl and Au-Te complexes have also been suggested for the dissolution of gold from rocks (*1*). However, which species is actually responsible for the dissolution has remained uncertain (*1*). Loucks and Mavrogenes have now identified the aqueous gold complex likely to be responsible for the dissolution as $AuHS(H_2S)_3^0$—consistent with gold's soft metal ion characteristics and the natural association of gold with the yellow mineral pyrite (FeS_2) termed "fool's gold." This result also answers the second question about gold deposits posed above: The more plentiful metals Pb, Zn, and Cu form soluble complexes with Cl



How gold deposits form. Schematic section of the crust illustrating channeling of hot fluids into shear zone faults where $AuHS(H_2S)_3^0$ destabilizes to precipitate metallic gold at 400° to 300°C and reduced pressure. Greenschist and amphibolite are characteristic sets of coexisting minerals stable under specific pressure and temperature conditions. Ninety-five percent of the vein gold mined globally is from deposits in the greenschist metamorphic environment, at about 400° to 300°C, whereas only 5% is from lower or higher temperature deposits.

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