The electron microprobe x-ray analyzer (the microprobe)—like the x-ray diffractometer, the emission spectrophotograph, and the mass spectrometer before it—is greatly changing petrologic and mineralogic investigation. With this instrument it is possible to make an accurate elemental analysis on a one-micron (0.001 mm) spot on a polished surface while simultaneously viewing the spot under a high-powered petrographic microscope. This makes it possible to correlate chemical composition with such physical properties of a mineral as zonal structure, grain boundaries, exsolution lamellae, or small inclusions.

The basic principle has been known for a long time and is, in fact, the basis for the x-ray tube. When a sample is bombarded by high-energy electrons, x-rays are excited in the sample with wavelengths characteristic of the various elements and with intensities, to a first approximation, proportional to the amount of the various elements in the sample. In the electron microprobe an electron beam is focused by magnetic lenses onto a polished surface of the sample to be analyzed.

The x-ray spectra produced are analyzed for wavelength by diffraction in a curved-crystal spectrometer and for intensity by a detector system. Analysis is carried out by comparing the intensity
of a characteristic wavelength of an element in the sample with the intensity of the same wavelength produced in a standard with a known concentration of the element. A spot, or a row of spots in a profile, may be analyzed simultaneously for several elements on different crystal-detector systems, or an area of the sample may be analyzed for a single element by systematic deflection of the beam as in a television tube. In addition, a single spot may be analyzed for many elements by scanning a range of wavelengths with the crystal-detector system and recording x-ray intensity versus wavelength.

Caltech’s microprobe is an Applied Research Laboratories EMX model, owned by the Jet Propulsion Laboratory and maintained and operated by A. A. Chodos of the geology division. Actual operation of the instrument is relatively simple, and it is used by graduate students and faculty alike in a wide variety of petrologic and mineralogic problems. Although a number of interesting problems have been undertaken for JPL, I can best indicate the usefulness of the instrument by describing some of the problems which have been undertaken by members of the division.

COMPOSITION OF COEXISTENT MINERALS

The chemical compositions of coexistent minerals in a rock are used by petrologists and geochemists to deduce the conditions under which the rock formed. Basically this is because a given array of atoms tends to aggregate into the configuration of lowest free energy for a given set of conditions. Hence an element (or an isotope) in a rock tends to be systematically partitioned between the mineral phases present, and the partition can be correlated with the conditions of formation, especially temperature. In the past such partition studies have required the mechanical separation of sufficient quantities of each mineral for chemical analyses, but truly pure separates of the phases are nearly impossible to attain. With the use of the microprobe, analyses are carried out in polished thin section on adjacent grains of the coexistent minerals; no mineral separation is required, and tiny inclusions of other minerals can be avoided.

A good example is provided by a study which has been made on muscovite, \([\text{KAl}_3(\text{AlSi}_3\text{O}_10)(\text{OH})_2]\) and its sodium analog, paragonite \([\text{NaAl}_2(\text{AlSi}_2\text{O}_10)(\text{OH})_2]\). The optical properties of these micas are so similar that they cannot be distinguished under the microscope, but x-ray diffraction studies had shown that the two commonly occur together. Although experimental work had provided information on the temperature dependency of their compositions, the similarity of all their physical properties had made separation for chemical analyses impossible.

In the electron beam scans (below) for K and Na in a single grain of finely intergrown muscovite and paragonite, the density of white spots is proportional to the concentration of the analyzed element. The inverse relationship between the concentration of K and of Na is evident and corresponds to a wedge-shaped boundary visible in the photomicro-

In the electron beam scans for K (left) and Na (right), the density of white spots is proportional to their concentration. The area shown, 55 microns on a side, is the same as the shaded area in the photomicrograph on the opposite page.
A photomicrograph of the muscovite-paragonite grain is shown above. A simultaneous analysis for K, Na, and Ca in a profile of spots (taken along the long linear mark across the grain in the photomicrograph) is shown below. Another mode of analysis is a chart giving the x-ray intensity for each wavelength; such a chart (above right) shows a portion of a wavelength scan for a point in the muscovite and a point in the paragonite portion of the grain in the photomicrograph.

The muscovite and paragonite were analyzed to a greater accuracy by accumulating counts for a longer time at two points about 15 microns apart. These analyses correspond to the following formulas: Muscovite, $[K_{1.7}Na_{0.1}Ca_{0.9}] [Al_{1.75}Fe_{0.05}Mg_{1.2}] [Al_{0.55}Si_{3.15}O_{10}] [OH]_{1.05};$ Paragonite, $[K_{0.67}Na_{0.39}Ca_{0.2}] [Al_{1.00}Fe_{0.05}Mg_{0.7}] [Al_{1.40}Si_{3.00}O_{10}] [OH]_{2.02}.$ Plotting the compositions of the coexistent muscovite and paragonite on a graph showing the temperatures at which muscovite and paragonite of a given composition were synthesized indicates that this metamorphic rock crystallized at a temperature somewhat above 500°C.

Similar investigations have shown that the minerals in many metamorphic rocks grew in chemical equilibrium with one another, since each of the elements is systematically partitioned between all of the phases present. Some elements, however, occur almost exclusively in a single mineral in the rock, suggesting that the crystal structure of that mineral has a nearly unique attraction for that element. For example, in garnet-bearing metamorphic rocks almost all the Mn$^{2+}$ in the rock is in garnet.

VALENCE STATE OF IRON AND MANGANESE

The x-rays produced in the sample are emitted as electrons drop from an outer shell of the atom into an inner shell. Since Fe and Mn in different valence states have different numbers and configurations of electrons in their outer shell, the wavelengths and intensities of the emitted x-rays vary slightly with the valence state. The variations can be seen in portions of wavelength scans for different minerals high in Fe$^{2+}$, Fe$^{3+}$, Mn$^{2+}$, or Mn$^{3+}$. Both the wavelength and the $L/\beta$ intensity ratio varies with the valence state. These relationships were developed during an investigation of interlayered green and red gneisses. The green coloring is due to abundant epidote $[Ca_2(Al, Fe^{3+})_2(SiO_3)_2(OH)]$, and the red coloring is due to abundant piemontite, which has the same crystal structure but which contains manganese. The analyses verified that the red color of piemontite is due to highly oxidizing con-

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Portions of wavelength scans showing $L_\beta/L_\alpha$ intensity for different minerals high in Fe$^{2+}$, Fe$^{3+}$, Mn$^{2+}$, or Mn$^{3+}$.

Conditions resulting in the presence of Mn$^{3+}$, rather than simply due to a high manganese content.

**COMPOSITIONAL ZONING IN MINERALS**

Some of the most interesting microprobe results are from studies of zoned minerals, since these give us information on the mineral growth history that can be obtained in no other way.

Garnet is a very common mineral in metamorphic rocks; it has a wide range of chemical composition expressed by its formula: $(\text{Fe}^{2+}, \text{Mg}, \text{Mn}, \text{Ca})_2(\text{Al}, \text{Fe}^{3+})_3(\text{SiO}_4)_3$. As indicated earlier, it has a very strong attraction for Mn$^{2+}$, and it has long been known that the garnet in low-grade metamorphic rocks is commonly highly manganiferous. Microprobe analyses have shown that garnet is almost invariably extensively zoned, typically with the pattern for Mn-variations shown at the right. The zoning indicates that, as the garnet crystal grew, each layer mantled the interior so that it did not equilibrate with the other minerals in the rock. This zoning pattern can be reproduced by a calculated model which assumes that Mn$^{2+}$ is strongly partitioned into garnet, that each layer as it grows takes up a constant high proportion of the remaining Mn$^{2+}$ in the rock, and that the amount of remaining Mn$^{2+}$ is constantly depleted by the growth of the garnet.

In some cases perturbations on this pattern can be related to variation in temperature or other conditions during the growth of the garnet.

**OTHER STUDIES**

Other studies that have been undertaken include the development of correction parameters which make possible the accurate analysis of complex silicates using simple silicates and oxides as standards. The homogeneity of the zircons used in age dating and the possible implications of their zoning have also been investigated. Microprobe analyses have been used in studies of the detailed crystallization history of a porphyry stock in the Death Valley region and of a layered diabase in Arizona. Coexisting minerals from an explosive peridotite pipe in northern Arizona have been analyzed, since such pipes may be derived from very deep within or below the earth's crust. Silicate inclusions in iron meteorites have been analyzed and identified by the microprobe. The chemical and mineralogic composition of the small teeth of chitons have been investigated. Analyses of various parts of the shells of fossils are used to study the conditions of animal growth.

These are only a sampling of the types of problems to which the microprobe is currently being applied. Within a few years the special capabilities of the microprobe will make it indispensable in most petrologic and mineralogic investigation.