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ELEMENT DISPERSION, ELEMENT CONCENTRATION, AND ORE DEPOSITS

by

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(3 figures)

This paper is dedicated with great affection to the memory of Paul Bartholomé.

1.- INTRODUCTION

Mineral deposits are volumes which contain one or more substances that can be extracted commercially. Such volumes may be filled with gases, liquids, solids or their mixtures. They can exist on bodies other than the Earth, but to date commercially extractable materials have been confined to the near-surface environments of the Earth, and it is unlikely that other parts of the solar system will become attractive as sources of raw materials until colonies are established on the Moon or on Mars.

The commercial extractability of elements and compounds depends on the size, shape, location, and constitution of the volume from which they are to be extracted. Most mineral deposits are distinguished by abnormally high concentrations of one or more elements or compounds in a portion of the Earth's crust that is amenable to mining. The Red Sea brines are an exception; they form a transition to minable brines in other parts of the world, to the oceans which now serve as a single, large mineral deposit for several elements, and to atmospheric and subsurface gases.

Mineral deposits are products of physical, chemical, and biological processes which together have determined the distribution of the elements and their compounds in the atmosphere, biosphere, hydrosphere, and lithosphere. Among these geochemical reservoirs the lithosphere is by far the most heterogeneous. Its heterogeneity is due in part to the operation of the many processes which separate and segregate elements and compounds today, and to the operation of these and other processes during much of Earth history. The Earth's crust has a long memory. The search for new mineral deposits within the Earth's crust should therefore be informed by our understanding both of the present-day workings of the Earth and of those processes which controlled the distribution of the elements in the distant past, when heat flow was considerably greater than at present, when tectonic processes were apparently different, and when living organisms were either absent or differed greatly from those of the present day. This chapter deals largely with the processes that tend to homogenize and to diversify the composition of the Earth's crust. We shall attempt to give a rather generalized view of the formation of mineral deposits as bodies at the extreme end of distribution patterns, of the manner in which these distributions have been generated and modifiel during geologic time, and of the implications of these matters for mineral exploration and resource availability.

2.- ELEMENT DISTRIBUTIONS IN CRISTAL ROCKS

The distribution of several of the major elements in igneous rocks is fairly close to normal (see for instance RICHARDSON & SNEESBY, 1922). The ratio of the concentration of these elements in their currently mined ores to their mean crustal abundance is typically less than ten. For iron and aluminium, the two metals for whose production the largest amount of money is spent annually, this ratio is only approximately 5 and 4 respectively. The cost of mining these metals will therefore never rise enormously because there is no necessity of extracting them from ores whose grade is orders of magnitude less than that of the corrently mined ores. The future real cost of extracting iron and aluminum from their respective ores will probably depend more on the balance between the increase in the

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prince of energy and the beneficial effects of technological innovations rather than on decreases in the grade of their ores, because there are essentially unlimited quantities of near-surface rock with concentrations of iron of aluminum that are within a factor of three of the present ore grade of these metals.

This is not true of the minor elements. Only about 20 elements have crustal abundances greater than 0.01 o/o (100 ppm); the remaining group of seventy-odd elements includes most of the important metals other than iron and aluminum. Copper, zinc, and lead are among its more prominent members. The distribution of these elements in crustal rocks is typically far from normal and generally close to log-normal (AHRENS, 1965). Figure 1, for instance, shows that the distribution of lithium in shales is log-normal or close to log-normal. This is reasonable from a purely intuitive point of view; the probability of finding a rock containing N times the mean concentration of a minor or trace element might be expected to be similar to the probability of finding a rock containing 1/N times its mean concentration. The proof of log-normality, however, demands either a sufficiently large data base or a sufficiently thorough understanding of the processes which control the distribution of particular elements so that a convincing case can be made for the log-normality of their distribution. Neither of these proofs is available for most trace elements. Most of the analytical data for trace elements do not extend beyond concentrations more than one or two orders of magnitude above or below their mean crustal abundance. The minimum ore grade of most of these elements lies beyond this concentration range (SKINNER, 1976a, p. 77), and an uncomfortably long extrapolation is generally required to connect the known crustal dispersion curve of ore metals to their ore-tonnage relationship. The assumption that the economically important trace metals are distributed log-normally over the entire concentration range between average crustal rocks and ores is therefore poorly based, and is probably wrong. As SKINNER (1976b) has pointed out, the distribution of ore metals may even be bi- or polymodal. It is obviously important, both for scientific reasons and for purposes of resource forecasting to define as carefully as possible the actual grade-tonnage relationship of ore metals between their concentration in presently mined ores and in average crustal rocks. A first attempt at deriving such a relationship for uranium within the United States will be described after a discussion of the major processes that dispense and concentrate the elements.

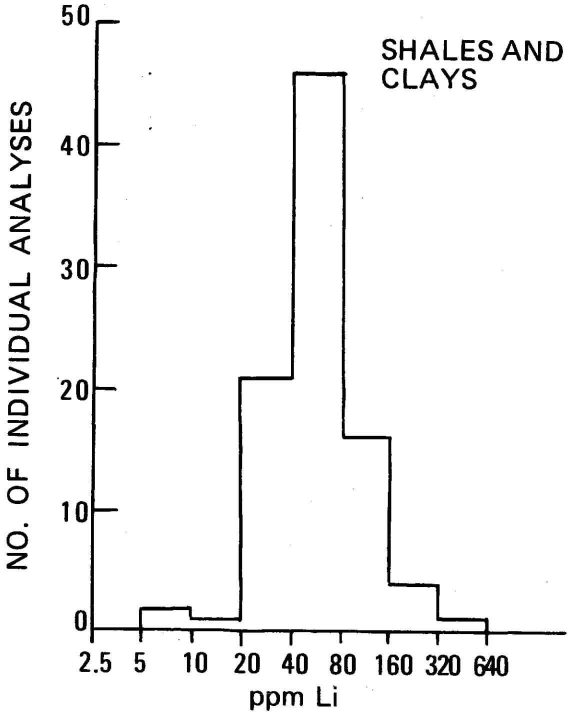

Figure 1.- The distribution of lithium in shales.

3.- DISPERSING AND CONCENTRATING PROCESSES

The crustal distribution of the elements is the sum of the effects of a multitude of processes which have acted repeatedly since the formation of the Earth to disperse and to reconcentrate the elements in the Earth's crust. The underlying driving forces for these processes have tended to remain the same : the outward transport of heat from the interior of the Earth and the input of solar energy. The intensity of these processes has varied with time, and the response of the Earth to the input of solar energy has been affected by the origin and evolution of life. The nature and the intensity of the forces which have dispersed and concentrated the elements and their compounds have therefore also varied with time. Nevertheless, the similarity between the most ancient rocks, both igneous and metasedimentary, and their modern counterparts attests to the essential conservatism of Earth processes, at least during the past 3.8 billion years. Recognition of this conservatism and of the modulation of Earth processes with time has been and will almost certainly continue to be an important ingredient in mineral exploration on a regional scale.

Concentration processes which lead to the formation of mineral deposits can operate in one of two ways : by selectively removing a large fraction of material from reasonably average rocks and thereby concentrating one or more elements in the residuum, and by direct concentration of a previously dispersed element or compound. Bauxite and lateritic nickel ores formed as a consequence of intense chemical weathering are examples of ores which owe their origin to processes of selective removal. The composition of the earliest metasedimentary rocks (see for instance HOLLAND, 1976) indicates that carbonation reactions during weathering were intense as long as 3.8 b.y. ago, and it seems therefore likely that bauxites and lateritic nickel ores have formed off and on during much of Earth history in parts of the continents where chemical weathering was particularly intense.

Most ore deposits have, however, been formed by processes which have brought together previously dispersed materials. These processes have almost invariably involved one or more fluid phases, and have been driven by a variety of physical, chemical, and biological mechanisms.

a) PHYSICAL MECANISMS

Gravity has played a major role in the formation of placer deposits in the formation of cumulate chromite deposits in ultramafic intrusives in the separation and accumulation of magmatic copper-nickel sulfide deposits and in the separation and accumulation of petroleum and natural gas. In contrast, magnetic and electric forces seem to have played a negligible role in processes of element concentration.

Since the Earth attained essentially its present size approximately 4.5 b.y. ago, g, the acceleration due to gravity, has presumably remained nearly constant for nearly all of Earth history. There is, however, fair evidence for considerable changes in the oxidation state of the atmosphere, and it seems likely that placers formed more than ca. 2.2 b.y. ago contained a larger proportion of minerals which are susceptible to rapid oxidation and dissolution under present-day conditions. The uraninite-containing placers at Blind River, Canada, and in the Witwatersrand and Dominion Reef series of South Africa are almost certainly examples of such preservation. It seems likely that other Archean and early Proterozoic placer deposits exist, and it may be worth looking for ancient placers which contain commercial quantities of base metal sulfides and other easily oxidized minerals.

b) CHEMICAL MECHANISMS

Chemical mechanisms of concentration are generally driven by chemical potential gradients, many of which owe their origin to temperature and pressure gradients. This is surely true of mechanisms related to partial melting, fractional crystallization, and liquid immiscibility in silicate and sulfide systems. It also applies to the boiling of magmas which seems to be largely responsible for the development of porphyry copper and porphyry molybdenum deposits, and perhaps for the origin of many post-magmatic hydrothermal base and precious metal deposits. However, vertical and horizontal temperature gradients within and around cooling intrusives also frequently generate systems of circulating meteoric and/or connate waters. Their circulation patterns, which are frequently, well documented by the geometry of their isotopic signatures, has led to the development of major hydrothermal base and precious metal deposits. Recent detailed work (PETERSEN *et. al.*, 1977; BIRNIE & PETERSEN, 1977; WU & PETERSEN, 1977) on the zoning patterns of metals within extinct hydrothermal systems of this type has shown that metal ratios can be used as a valuable exploration tool. They also bid fair to permit a more quantitative treatment of the paleohydrology of such systems by the application of the techniques of hydrologic modeling, which have been pioneered by CATHLES (1977) and FEHN & CATHLES (1979). It now seems likely that the thermal structure required for the development of major hydrothermal ore deposits is present in the vicinity of many intrusives and within the deeper parts of many volcanic complexes, and that the development of ore deposits in such settings depends rather critically on the nature of the hydrothermal flow regimes in such settings. In particular, a relatively large proportion of the total flow must apparently be channeled through a rather small number of pipes and/or fractures. If the flow is too diffuse, mineralization becomes too disperse and does not reach ore grade.

The chemistry of the transport and deposition of ore minerals in hydrothermal systems is reasonably well understood, although there is still a serious lack of solubility and other thermodynamic data, and a virtual absence of data on the kinetics of reactions at elevated temperatures and pressures. Ore deposition is frequently brought about by a decrease in the solubility of ore minerals in the direction of solution flow due to a decrease in temperature and/or pressure, by reactions between dissolved species within hydrothermal solutions, by boiling, by mixing, and by reactions of solutions with wall rock minerals or with previously deposited hydrothermal minerals. The sum total of all these reactions is frequently very complicated.

Computer modeling as developed by HELGESON (1968, 1970) has proved particularly helpful in tracing the chemical evolution of hydrothermal systems. Helgeson's techniques are currently being applied to defining the chemical changes that accompany boiling in hydrothermal systems, especially the possible effect of these changes on the formation of porphyry copper and bonanza gold-silver deposits.

Reactions between oxidized species in solution and reducing agents either along the flow path or in fluids with which mixing can take place are important for the development of many hydrothermal uranium deposits (see for instance RICH, HOLLAND & PETERSEN, 1977). The recognition of this fact has had a strong impact on prospecting for such deposits during the past 30 years. The association of hydrothermal uranium deposits with uraniferous granites has proved similarly important, apparently because such granites generate enough heat to drive hydrothermal systems which are sufficiently intense to produce the associated uranium deposits (FEHN, CATHLES & HOLLAND, 1978).

In some hydrothermal systems seawater is the dominant fluid. This is true particularly in the Reykjanes geothermal system of Iceland, and in submarine geothermal systems such as those discovered near the Galapagos spreading center (CORLISS *et al.*, 1979) and probably in those near 21°N at the crest of the East Pacific Rise. The involvement of seawater in the development of at least some parts of Kuroko deposits seems beyond reasonable doubt (FARRELL, HOLLAND & PETERSEN, 1978). Whether and how much magmatic-hydrothermal water contributed metals from depth in these deposits is still a matter of dispute. It will be most instructive to compare the origin of Kuroko deposits with that of the recently discovered sulfide deposits on the East Pacific Rise at 21°N. Other sulfide deposits of this type are almost surely being formed along volcanically active portions of fast spreading ridges. Whether the mining of such deposits will ever be commercially feasible is not clear. However, the extensive accumulations of metalliferous sediments near the East Pacific Rise between the Equator and 20°S may well be a complement of base metal sulfide deposits on the Ridge, and thermally anomalous regions in areas of back arc spreading in other parts of the world ocean may be similarly interesting targets for exploration.

It seems very likely that mineral accumulations have formed at numerous places along the 50.000 km of mid-ocean ridges, because ridges are such ideal locales for the circulation of seawater through the oceanic crust. If such deposits are preserved during the movement of new crust away from spreading ridges, large parts of the deep ocean floor might ultimately become targets for mineral exploration. The sea floor may then turn out to be of interest for several materials in addition to manganese nodules.

Even in the absence of hydrothermal processes, sedimentation in the oceans and the diagenesis of marine sediments make the oceans a major source of mineral commodities. However, with the important exception of the formation of evaporites , most of the processes which concentrate one or more elements or compounds to commercial levels involve living organisms and are best discussed under that rubric.

c) BIOLOGICAL MECHANISMS

The biosphere plays and has played a role in the nature and operation of near-surface processes that is out of all proportion to its mass. The disposal of the river input of Ca^{+2}, HCO_3^-, and H_4SiO_4 to the oceans is mediated almost entirely by marine organisms, and the marine chemistry of nitrogen, phosphorus, silica, and of many trace elements is determined largely by biologic processes. Hence, the distribution of limestones, diatomites and phosphorites is strongly linked to biologic processes; the success of exploration for phosphate deposits owes much to our understanding of the interplay between the upwelling of nutrient-rich water masses, biologic productivity, and the concentration of phosphate by diagenetic processes.

The concentration of organic remains in carbon-rich deposits, and the subsequent development of oil gas accumulations is somewhat outside the scope of this report; however, the concentration of significant quantities of metals in black, carbonaceous, frequently petroliferous shales falls within its purview. It is likely (HOLLAND, 1979) that seawater is normally the source of the metals enriched in these shales, and that much of the process of concentration takes place not during the lifetime of the organisms whose remains are partly preserved in black shales, but during and after sedimentation by extraction from overlying seawater and immobilization by adsorption, precipitation and coprecipitation with sulfides and oxides, and probably by other mechanisms which are still poorly understood. In such sediments the ratio of the excess quantity of a given metal to its concentration in present day seawater tends to be similar for several enriched elements, and is frequently between 1×10^5 and 5×10^5 (HOLLAND, 1979). However, some elements, most notably molybdenum, are underconcentrated in black shales by this criterion, presumably because they are partially remobilized during early diagenesis and diffuse back from marine sediments into the overlying water column.

Some black shales are already of commercial interest, and will probably become progressively more attractive because of the combined effect of the potential for the recovery of several metals and of the energy potential of the contained elemental carbon and petroleum; the prospective ore tonnages of such shales are frequently very large indeed. A thorough analysis of the distribution of metalliferous black shales within former marine basins, of the mechanisms by which such shales are formed, and of geologic periods that were particularly favorable for the formation of such sediments therefore seems a worthwhile undertaking. The available data suggest that the concentration of the trace metals in seawater has been surprisingly constant during the Phanerozoic era. There are very few pertinent data for the Precambrian era.

Although the behavior of trace metals in the Precambrian oceans is largely unknown, it is virtually certain that the marine geochemistry of silica was quite different in the Precambrian than during the Phanerozoic era, and that these differences are reflected in the nature of Precambrian sedimentary ores. Cherts associated with the extensive Proterozoic Lake Superior-type banded iron formations, which are not related to nearby volcanism, are best explained by concentrations of silica in seawater well in excess of its present day concentration range. This is readily explained by the absence of silica-secreting organisms during much, if not all, of the Archean and Proterozoic eras, and by the requirement that river borne silica was removed from the oceans at rates which were probably similar to those of the present day. A relatively high (30-100 ppm) SiO_2 concentration in the Precambrian oceans might also explain the chemistry and mineralogy of the rich, presently unique zinc-iron-manganese ores at FRANKLIN and STERLING HILL, N.J. In areas where hydrothermal solutions emerged into a middly oxidizing, silica-rich ocean, hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) might have been deposited together with iron and manganese oxides and/or carbonates. During metamorphism such mineral assemblages could have been transformed into the assemblages of the famous New Jersey zinc ores (FRONDEL & BAUM, 1974). If this explanation is correct, then it seems likely that other, perhaps unmetamorphosed, ores of the Franklin type remain to be discovered in Precambrian sediments; such ores could have been missed, in part because the physical properties of hemimorphite are rather commonplace.

4.- THE CRUSTAL DISPERSION OF URANIUM

The crustal dispersion of many trace elements extends from concentrations in the parts per billion range to concentrations in the range of tens of percent. Uranium belongs to this group of elements. Volumes on the order of a few cubic centimeters to a few cubic meters may consists of nearly pure uraninite, and hence may contain up to ca. 88 o/o uranium. In extremely rich portions of mines, uranium grades can reach values in excess of 10 o/o. However, the grade of most uranium ores today is well below 1 o/o, and is frequently less than 0.1 o/o. In the future, rocks containing below 0.05 o/o (500 ppm) uranium will be commercially attractive.

The development of nuclear power depends on the future availability of uranium; there is, therefore, a great need for reasonably reliable estimates of the resource base of uranium. Such estimates are difficult to make, because most ore bodies of uranium are small, and because their distribution tends to be erratic at depths of less than 500 m and largely unknown at greater depths. Nevertheless, it is possible to make reasonable estimates of the minimum tonnages of uranium ore within the range of grades which are currently mined, and gross estimates of tonnages between these and average crustal rocks, especially in areas like the U.S.A. where analytical data for the distribution of uranium are reasonably abundant. Figure 2 from TULCANAZA & HOLLAND (in preparation) is a first attempt at such a distribution curve. The abscissa represents the concentration of uranium on a logarithmic scale from 0.1 ppm to 100 o/o (10^6 ppm). The ordinate represents the estimated numbers of tons of rock within the upper 1 km of crust below the U.S.A., which have a uranium content between the indicated concentration limits. This scale is also logarithmic, because the range of tonnages is much too large for a meaningful representation of the data on a linear scale. It goes without saying that the enormous tonnage range precludes the use of this diagram for anything but the roughest indication of uranium resources within the United States.

The total mass of rock in the upper 1 km of crust beneath the continental U.S.A. is ca. 2.7×10^{16} tons. The tonnage distribution of uranium in the category of average crustal rocks was derived from this figure, from estimates of the lithology of rocks in the uppermost

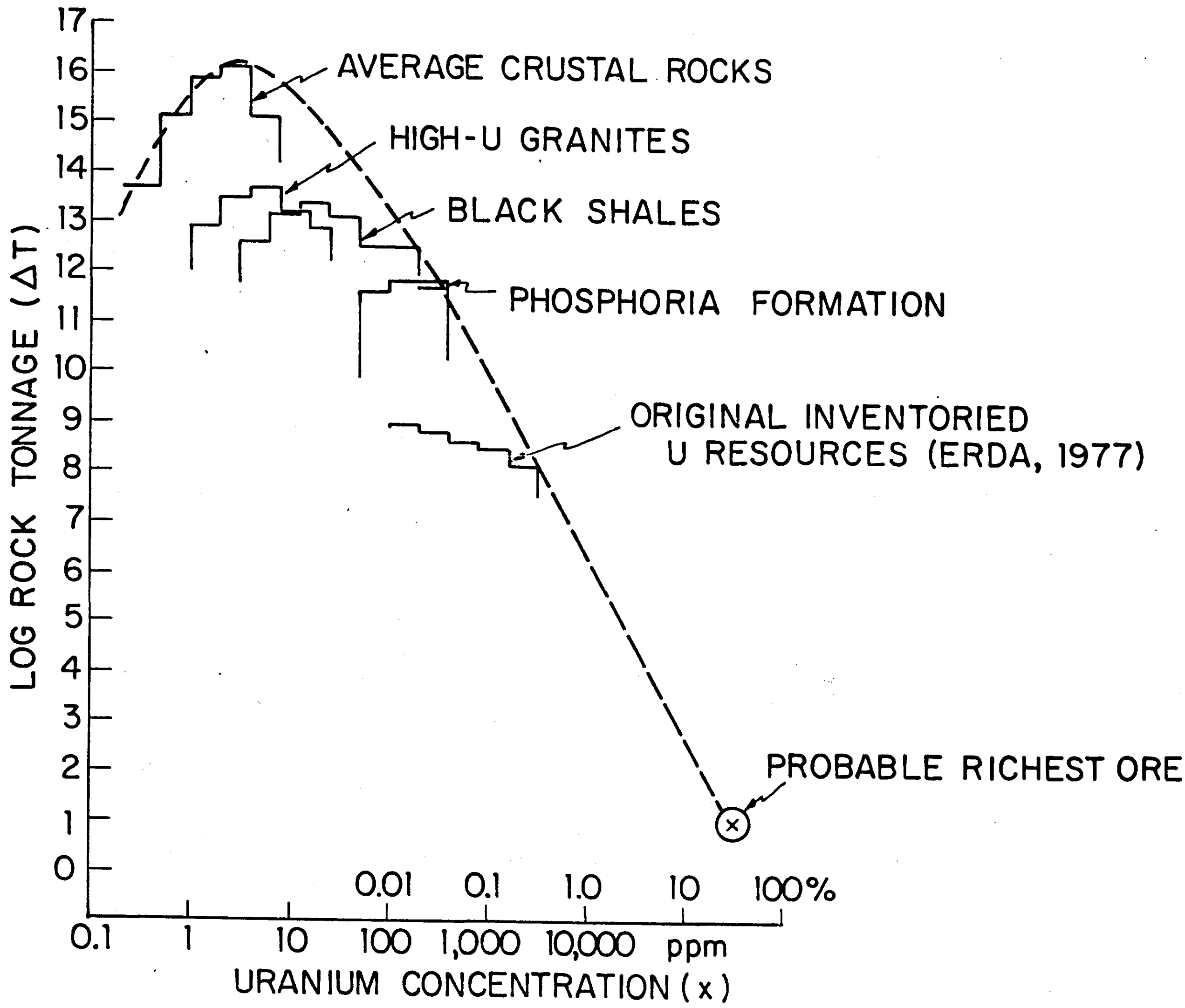

Figure 2.- Tonnage-grade data for uranium in the top 1 km of crust below the continental U.S.A.

1 km of crust, and the distribution of uranium in the several rock types. The tonnage distribution in the category of high-U granites is based on data for uranium in uraniferous granites in the Colorado Front Range, the Boulder Batholith, and the Granite Mountains. The distribution of uranium in black shales includes units which range in location from Eastern Tennessee to Texas and Montana. The Phosphoria Formation distribution is based on the distribution of uranium in this formation in the western part of the U.S.A. The distribution of grades in the category of original inventoried U resources was taken from the 1977 ERDA report on this subject. The indicated grade and tonnage of the probable richest ore is an estimate based on conversations with mining geologists.

The several distributions in this figure have rather different meanings. The tonnage-grade relation for average crustal rock is anchored by the area of the U.S.A. and by the 1 km depth which was chosen for the calculations. The actual contained uranium in average crustal rocks is therefore almost certainly close to the indicated value in Figure 2. The other distributions, however, represent minimum values for the uranium content in the several categories. Not all high-uranium granites, black shales, or phosphorites are represented in their respective grade-tonnage curves. The category of original inventoried U resources includes only resources which were known when the 1977 ERDA report was written. The tonnage of probable richest ore is a minimum value for related reason. The true tonnage of uranium in these several categories is therefore surely greater than the tonnages indicated in Figure 2. However, since the tonnage scale is logarithmic, the average shape of the distribution curve will probably not be changed dramatically by the acquisition of new analytical data and discoveries of additional uranium ores.

The data in Figure 2 reinforce several impressions.

1. The tonnage of uranium ores is completely trivial compared to the tonnage of uranium in average or nearly average crustal rocks. The shape of the uranium distribution curve is therefore determined more by the efficiency of the concentrating processes than by the availability of uranium. This seems to be true of most other ore metals as well.

2. The actual grade-tonnage relationship is complex, but does not appear to be bi-or polymodal. The large gap between the dashed envelope and the distribution of uranium in the category of original inventoried resources is probably in part due to a lack of interest and hence an underestimation of the quantity of uranium in mineralized ground containing only a few hundred ppm of uranium. The true slope of the tonnage-grade relationship may well be critical for

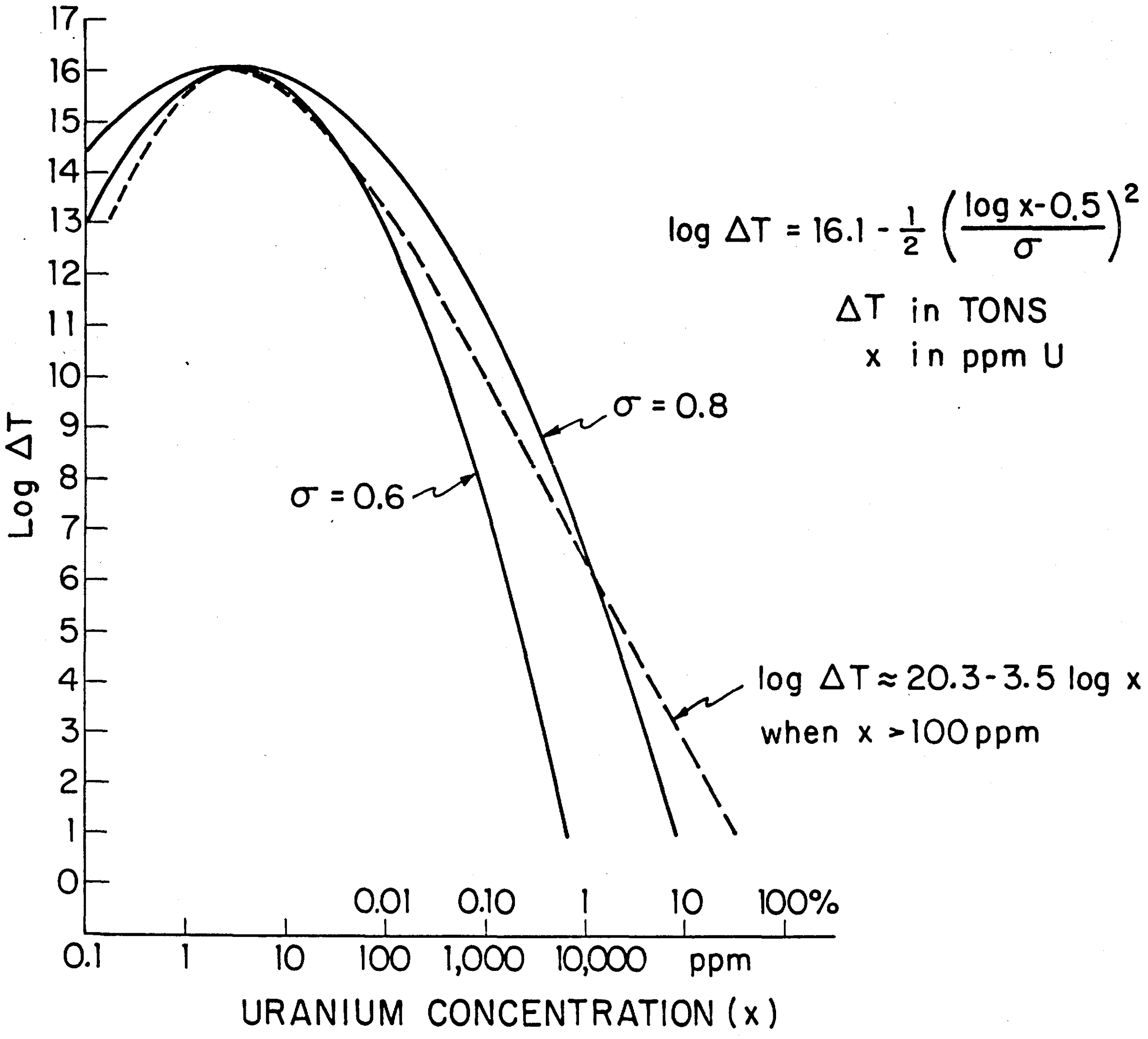

Figure 3.-
Attempts to fit log-normal distribution curves to the envelope of the tonnage-grade data for uranium in Figure 2

uranium mining in the U.S.A. during the next decades.

3. Phosphorites will almost certainly be the next, major source of uranium in the U.S.A. Uranium as a byproduct of phosphate mining can apparently contribute only a rather minor fraction of the projected uranium needs. If phosphorites do become a major source of uranium, very large quantities of byproduct phosphate should become available for the fertilizer industry.

4. Black shales could become important sources of uranium, especially if black shales comparable to the Swedish Alum shales were discovered, and if the simultaneous use of energy and the extraction of several metals from black shales becomes a reality.

5. Currently, high-uranium granites do not look attractive as sources of uranium.

The significance of the dashed envelope in Figure 2 is perhaps debatable. However, it can be used at least to suggest an answer to the question whether the distribution of uranium is log-normal over the entire concentration range of Figure 2. Figure 3 is an attempt to fit log-normal distributions to the envelope. The result is unsatisfactory. At uranium concentrations in excess of 100 ppm the envelope can be described by the equation

$$\log \Delta T \approx 20.3 - 3.5 \log x$$

where x is the concentration of uranium in ppm. The form of this equation is quite different from that of a log normal distribution; it is therefore not surprising to find that log-normal distributions can be made to fit either the distribution of uranium in average crustal rock ($\sigma = 0.6$) or the distribution in ores ($\sigma = 0.8$), but not both. This result should act as somewhat of a deterrent to the use of resource predictions which are predicated on log-normal distributions of the ore metals.

5.- SOME IMPLICATIONS FOR THE FUTURE OF MINERAL RESOURCES

The grade-tonnage diagram of Figure 2 invites a vision of progressively lower ore grades and of ever higher raw material production costs. Although this vision is probably correct, it may be possible to keep the rate of increase of the real cost of raw materials at fairly modest levels.

PETERSEN & MAXWELL (1979) have shown that the real cost of most metals proceeds through three stages : an initial period, when production rates are increasing rapidly and unit costs are decreasing due to technological progress and economies of scale, a middle period, when unit costs are nearly constant, and a later period, when the rise in production costs exceeds the effect of economies due to improved technology and increased production. Aluminum has been the most spectacular example of a "new" metal, petroleum and natural gas the most spectacular examples of "new" fuels in the 20th century. It seems likely that advances in metallurgy and in material science will bring additional new materials to the fore, and that their evolution will serve to slow the increase in the total cost of raw materials.

Recycling and substitution should also be of help, but the stability of energy prices may well turn out to be the single most important requirement for reasonably stable production costs of metals during the next two decades.

Beyond this period the discovery of new ore deposits, particularly deposits which are large and rich, is apt to be of critical importance. The recent discoveries of large, high grade uranium deposits in Canada and Australia have followed a renaissance of interest in uranium and a dramatic increase in the price of this metal. In the U.S.A. it may be necessary to adopt new exploration strategies to make discoveries of similar magnitude. The Precambrian basement under the cover of Phanerozoic sediments in the mid-continent region is a potential target for a variety of major mineral deposits. The discovery of a Blind River-Elliott Lake uranium or uranium-gold deposit, of a Bushveld chromium-platinum deposit, or of extensive deposits of banded iron formation could be of considerable importance for the U.S. mineral industry. Smaller exploration targets would be hard to find, and their search would be hard to justify. If mineral and element dispersion patterns along or near the Precambrian-Phanerozoic contact are sufficiently extensive that they can be detected by a modest number of drill holes, such ores might be sought as part of a Continental Scientific Drilling Program (U.S. Geodynamics Committee, 1979).

Deep ocean mining is apparently becoming a commercial reality. The possibility of mining sulfides at the ocean floor was discussed earlier. This is almost certainly a good way off, but is worth keeping in mind. Similarly, the possible presence of ores of chromium and platinum on the sea floor deserves some thought, since ores of these metals are characteristically associated with mafic and utramafic rocks, which dominate the petrology of the oceanic crust.

Finally, it is worth pointing out that a gradual movement to lower grades along the grade-tonnage curve of an element may reach the point where ocean water itself becomes a competitive source for the element. Magnesium is a case in point, and it may be possible before long to extract several trace metals from the oceans on a commercial basis. Since the oceans are essentially infinite reservoirs of nearly constant grade, grade-tonnage curves such as Figure 2 are of only modest economic significance once extraction from seawater becomes attractive. It goes without saying that seawater would become particularly attractive as a source of raw materials if large scale desalination of seawater were to become economically attractive as a source of water in arid parts of the world.

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