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Ore Metals Through Geologic History

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Summary. The ores of chromite, nickel, copper, and zinc show a wide distribution over geologic time, but those of iron, titanium, lead, uranium, gold, silver, molybdenum, tungsten, and tin are more restricted. Many of the limitations to specific time intervals are probably imposed by the evolving tectonic history of Earth interacting with the effects of the biomass on the evolution of the earth's surface chemistry. Photosynthetic generation of free oxygen and "carbon" contributes significantly to the diversity of redox potentials in both sedimentary and igneous-related processes of ore formation, influencing the selection of metals at the source, during transport, and at the site of ore deposition.

Ore deposits are rocks in which natural processes have brought about a sufficient concentration of commercially useful elements that they may be available for economic extraction. Depending on the element, ore grade requires natural concentrations ranging from about five times to many thousands of times the average crustal abundance. In a few cases, the concentration process may involve only a few major steps, such as settling of early-formed chromite crystals in an ultrabasic (magnesium- and iron-rich) magma, but generally ores are the products of much more complicated systems of rock-forming events taking place over substantial intervals of geologic time.

Most ore deposits were formed at or near the interface between the solid earth and its fluid envelopes, either at the earth's surface or not far below it. This is the zone of interaction between the solar heat flux, which powers most processes of weathering and sedimentation, and the earth's interior heat flow, which drives most tectonic and igneous processes. Within this zone, natural chemical and thermal gradients are steep and variable, and reactions are also tempered or enhanced by the activity of the biomass.

Solar energy powers various kinds of hydraulic pumps. Locally coupled with ocean tides, these pumps regulate mechanical and chemical processes of weathering, erosion, and sedimentation, which are powerful mechanisms for the direct concentration of ores. But perhaps an equally important route of solar energy influence has been through the activities of the biomass. The sun supplies energy for photosynthesis. Oxygen is liberated during this endothermic process, with the generation of organic compounds whose eventual degradation provides carbon and hydrocarbon, which becomes "fixed" in sedimentary rocks. The fixation of carbon and liberation of oxygen generate a colossal energy storage cell, the cumulative effects of which have been profound in the history of the earth.

The resulting divergence or "spread" of oxidation potential has provided much of the chemical diversity that may be unique to the earth among the planets. The effect of this divergence on surface sedimentary environments is obvious, providing for the proliferation of sedimentary ore-forming environments as well as for accelerated evolution of the biomass. But the carbon fixed in sediments also affects igneous-related ore-forming processes for such elements as tin and tungsten if continental crustal rocks containing carbon are subjected to partial melting.

The tectonic evolution of the earth is basically a response to changes in the rates and mechanisms of heat generation and heat dissipation over geologic time. Heat loss from the earth's interior is chiefly by igneous activity, and currently this is localized principally (but not exclusively) near crustal plate boundaries. For earlier periods of the history of the earth, the patterns of heat loss must be judged from the distribution of rocks and ores of all types—igneous, sedimentary, and metamorphic—as they were assembled into structural arrays which may diverge significantly from current patterns.

The temporal distribution of metals in various petrologic associations and tectonic habitats is shown in Tables 1 and 2 (*1*).

Chromite and Nickel

Chromite cumulates and nickel sulfide ores are closely associated with ultramafic and mafic rocks whose magmas probably originated as first-cycle (*2*) partial melts of the mantle. Much of the range in composition of the magmas may result from the degree of partial melting, with basaltic magmas dominant both as flows and as intrusions. Large intrusions, such as the Bushveld Complex of South Africa, generally crystallized slowly enough to differentiate internally, with early-formed crystals settling as cumulate layers in the lower part of the complex. Chromite layers of this type, some with great lateral persistence, contain such enormous tonnages of chromite

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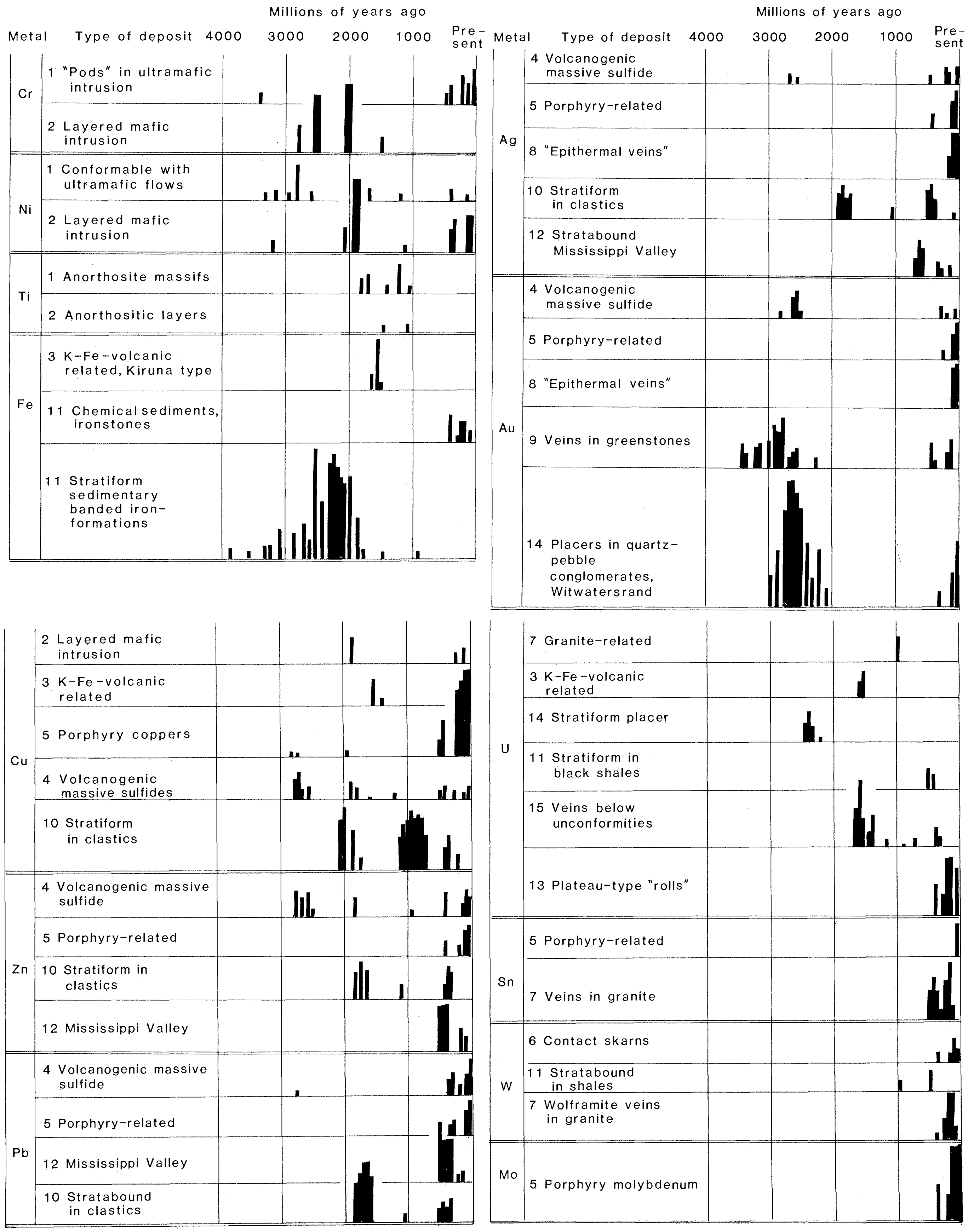
Table 1. Temporal pattern of distribution of types of ores through geologic time. The bars show the approximate proportion of the ores of each metal at the age indicated, compared to the total for that metal. The scale is different for each metal. The number ahead of each designation of type of deposit refers to the cryptic description of that type in Table 2. The major divisions of geologic time, as used in this article, are as follows: Archean, ~3900 to 2500 m.y. (~3000 m.y. in South Africa) ago; Early Proterozoic, 2500 to 1800 m.y.; Late Proterozoic, 1800 to 600 m.y.; and Phanerozoic, 600 m.y. to the present.



ore that only a few of the best (like the Bushveld, 2000 million years (m.y.) old, and the Great Dyke, 2500 m.y. old) will probably dominate the market for many years to come.

Chromite is also an ore mineral in ultramafic massifs (*3*), which are common in Phanerozoic orogenic belts (400 m.y. to the present). Relict layering is locally present in these bodies, but the chromite is generally in irregularly elongate pods (podiform) having mosaic texture. This suggests the growth of grains after accumulation but still at magmatic temperatures. Dunite is the main host rock, but serpentinization of the olivine is commonly complete.

There are no important podiform chromite ores in the Proterozoic, but there are several Archean examples, such as the large deposit at Selukwe, in Zimbabwe. Selukwe chromite ore bodies not only have the morphology of Phanerozoic pods, but their chromium spinel is similarly higher in chromium and magnesium than spinel in most of the later layered complexes. Cotterill (*4*, p. 186) concluded that "the form and distribution [of the pods of chromite] were initiated by buckling of the floor of the magma chamber at the time of accumulation." Considering the mosaic texture and uniform composition of both chromite and olivine, Phanerozoic podiform chromite ores probably owe their shape to deformation of ocean crust during or shortly after the original emplacement of the massifs.

Nickel sulfide ores are also found in mafic and ultramafic rocks, but the compositions, tectonic environments, and temporal distribution patterns are different from those for the chromite ores. As a source of nickel, Sudbury, at mid-Proterozoic (1840 m.y.), dominates the zoned noritic intrusions of the Precambrian. Other giant ore bodies of similar metal content are the Triassic Norilsk in the U.S.S.R. and late Paleozoic Jin Xiang in China. These two are apparently internally differentiated thick gabbroic sills. The Sudbury "irruptive" is a floored intrusion also, with the sulfides located mostly at or near the "bottom," but there is considerable dispute over the mechanisms of emplacement and zoning, which may have been energized by a large impact.

Kambalda-type nickel sulfides (*5*) are present as interflow layers below or between komatiitic (magnesium-rich) ultramafic lava flows, which commonly show skeletal olivine (spinifex) textures. Such olivine-rich flows are now known to be fairly common in Archean greenstone assemblages, but nickel has been found in commercial quantities only in a few places.

Taken as a group, chromite and nickel ores in mafic and ultramafic rocks are spread over a wide range of geologic age, from about 3400 m.y. virtually to the present. Both chromite and nickel came on strong again in the Phanerozoic after a period from about 1800 to 600 m.y. (Late Proterozoic) of minimal incidence. Conceivably, erosion has not penetrated deeply enough in some areas to expose the chromite horizons of layered complexes younger than the Bushveld, but the sudden proliferation of podiform chromite in the Phanerozoic, and the preference of Kambalda-type ores for Archean greenstones, can hardly be the result of selective exhumation or obliteration by erosion.

The Titanium-Anorthosite Connection

Massive ilmenite ($FeTiO_3$) ore lenses, such as Allard Lake, Quebec, are in anorthosite (calcium feldspar–rich) massifs, in much the way that massive podiform chromite tends to occur with dunite massifs. The texture of the ilmenite is mosaic, like the chromite in podiform chrome. Hematite is present as exsolution lamellae out to the edge of the ilmenite grains. This feature suggests mosaic growth at magmatic temperatures after settling, before appreciable cooling.

Elaborating the analogy with chromite, one also finds ore-grade titanium concentrated as titaniferous magnetite in some layered complexes at the level of calcium-rich silicates (the anorthosite layers). Both massifs and layered anor-

Table 2. The types of mineral deposits as used in this article, with short descriptions and an example of each type. The numbers are used to identity the type in Table 1.

Type	Example
1. Ore in ultramafic (Mg-rich) rocks	
In komatiite flows with skeletal olivine nickel sulfides in interflow sheets	Kambalda Ni
In serpentinized dunite (olivine) massifs, "podiform chromite" ore bodies, deformed	Masinloc Cr
2. Ore in layered mafic intrusions	
Internally differentiated plutons, presumably floored	Bushfeld Cr Sudbury Ni
Thick sills, internally layered	Norilsk Ni
3. Ore with alkali and ferric Fe-rich flows and granitoid intrusions and pyroclastics	Kiruna Fe
4. Volcanogenic massive sulfides deposits; part of volcanic edifice in crater or on flank; massive pyrite or pyrrhotite, or both	
On oceanic basalt (ophiolites common)	Cyprus Cu
Fumarolic on rhyolite — Precambrian	Noranda Cu, Zn
Phanerozoic	Kuroko Pb, Zn, Cu
5. Porphyry-related subvolcanic plutons, diorite to quartz monzonite composition	
Porphyry coppers	Chuquicamata Cu, Mo
Porphyry Mo	Climax Mo
6. Contact metamorphic skarn; limestone invaded by granitic or porphyry pluton	Bingham Cu, Zn, Pb Pine Creek W
7. Veins in granitoids, generally quartz-rich	Southeast China W Cornwall Sn
8. "Epithermal" veins and replacements; shallow veins in volcanic environment, generally rhyolitic porphyry or bimodal suite	Goldfield Au Comstock Ag
9. Veins in greenstones and turbidites, mainly quartz with minor sulfide and locally tellurides; some without quartz in carbonate alteration	Hollinger Au Bendigo Au
10. Stratiform sulfides in classic sediments; generally marine, in large basin or shelf; not part of a volcano, though may be some volcanic provenance	Katanga Cu Kupferschiefer Cu, Ag Sullivan Pb
11. Stratiform ores in chemical sediments, only minor clastics	Banded Fe formations
12. Strata-bound in carbonate rocks; not necessarily precipitated with host rock, but broadly confined to particular stratigraphic ranges	Mississippi Valley Pb, Zn
13. Strata-bound in clastics; crosscutting in detail but favors particular stratigraphic horizons	Plateau uranium U
14. Placers; mechanically concentrated heavy minerals, generally in coarse clastics; may be some recrystallization	Witwatersrand Au, U
15. Residual from weathering, or transported by weathering; veins below unconformities	Athabaska U

thosites penetrate continental crust, and their emplacement is strongly clustered in the upper Proterozoic between about 1700 and 1000 m.y. (*6*), the period of apparent minimum activity for chromite and nickel.

The Base Metals: Copper, Zinc, and Lead

Sulfide ores of copper have the widest range of habitat and the widest range of geologic age of any major metal. Copper is as abundant as nickel in first-cycle mafic intrusions such as Sudbury. It is a major metal in igneous-related hydrothermal systems of numerous types, such as the porphyry coppers, but stratiform ores now supply about 40 percent of the world copper production.

Copper is also a major metal precipitated with iron sulfide at present seafloor hydrothermal vents. Most examples of this class of volcanogenic massive sulfides, such as the deposits in Cyprus, are probably on Phanerozoic first-cycle ocean ridge basalts. Copper is also a principal ore metal in volcanogenic massive sulfide ore bodies (group 4 in Table 2) deposited on the upper felsic (rhyolitic) members of undersea volcanic piles. Zinc and lead are associates of copper in Phanerozoic volcanogenic deposits, as in the Kuroko deposits of Japan. But copper and zinc, with very little lead, are the main ore metals in Precambrian massive sulfides.

On the average, the Precambrian deposits are much larger than the Phanerozoic, the fabulous Kidd Creek ore body near Timmins, Ontario, possibly reaching 200 million metric tons. Archean massive sulfides are characteristically atop cyclical ultramafic-to-felsic volcanic piles in greenstone belts, especially in North America where the age range is from 2800 to 2500 m.y. (*7*). They are scarce in the older greenstone belts of South Africa and Australia, where the proportion of ultramafic units is generally greater.

There was a mid-Proterozoic resurgence of Archean-style massive sulfide-type mineralization, particularly in North America. The large Jerome, Arizona, and Crandon, Wisconsin, ore bodies, for example, and deposits in the Churchill province of Canada, are in volcanic piles that include thick felsic pyroclastics over basaltic bases but without visible ultramafics. These may be in continental-margin volcanic-orogenic belts.

Archean massive sulfides (*7*) are the oldest ore bodies of zinc. The deposition of abundant zinc with copper atop the felsic volcanics contrasts with the relative scarcity of zinc in Cyprus-type ore bodies where only oceanic basalt is hydrothermally leached. Second-cycle, felsic partial melts of basaltic crust apparently preconcentrate the zinc to make it available to convecting hydrothermal seawater.

The paucity of lead in Archean volcanogenic ore systems is anomalous, in view of the fact that lead is a prominent metal, with zinc, in Phanerozoic ores of the same type. The observation is reinforced by the fact that there are only a few small lead-rich deposits of any kind prior to the mid-Proterozoic. This is in striking contrast to the period just after the mid-Proterozoic, between about 1800 and 1500 m.y. ago, which has accounted for nearly one-third of the world's production of lead. Broken Hill, Mount Isa, and McArthur River in Australia and Sullivan, British Columbia, are the giants in this group, and they are all stratiform deposits with the ore in marine clastic sediments. Sullivan shows an alteration root and a nearby rift, and in the others volcanics may be part of the provenance of the basins in which ores were deposited as chemical sediments. But none of these deposits is part of a volcanic edifice like the volcanogenic massive sulfides.

After the surge of stratiform lead between about 1700 and 1500 m.y. ago, there were very few important lead deposits formed for about a billion years until the advent of the Paleozoic stratiform and Mississippi Valley–type ores. Instead of major lead deposits, the basins of the mid–Late Proterozoic were hosts to some of the world's greatest copper deposits, such as the African Copper Belt of Zambia and Zaire (*8*). These stratiform deposits are in a hinged basin that was tectonically active while shallow-water sedimentation was going on. Cobalt is associated with the copper, and crosscutting pipe deposits such as Kipushi and Shinkolobwe contain high-grade ores, including lead and uranium on the hinged side. In rocks of broadly similar age on the western side of the Kalahari, the Tsumeb pipe (*9*) contains the world's greatest concentration of germanium. The mechanisms of mineralization of such pipes are very poorly known, especially in relation to the selectivity of their metal content.

Probably more than half the world's total copper ore resources are in stratiform deposits. These started with Outokumpu in Finland and Udokan in Siberia about 2000 m.y. ago, continuing intermittently into the Phanerozoic with Dzhezkazgan, U.S.S.R., Lubin, Poland, and the Kupferschiefer of the Erzgebirge. But, except at Mount Isa, although stratiform copper is both older and younger than the mid-Proterozoic lead group, copper and lead are not often in the same deposit. Gustafson and Williams (*10*) regard this as an indication that the methods of supply of the two metals are different, with the higher grade lead more closely related to rift-controlled hydrothermal sources. Copper is usually much more dispersed and lower grade, perhaps more dependent on sedimentary controls. Although by no means exclusively, zinc tends to follow copper in igneous-related hydrothermal environments and to follow lead in stratiform sedimentary environments. Both types of terranes are well-exposed throughout the world, so it is unlikely that the volcanic type could have been selectively diminished by erosion from Proterozoic rocks except for the group around 1800 m.y., while they are so well-preserved in the Archean before 2500 m.y. and in the Phanerozoic from 600 m.y. until now.

Large basins were formed on stabilization (cratonization) of continental crust. This process apparently started in what is now southernmost Africa (at about 3100 m.y.); elsewhere it indexes the end of the Archean at about 2500 m.y. Selective erosion could not readily account for the absence of stratiform base-metal sulfide deposits from rocks older than 2000 m.y. and their abundant preservation in the upper Proterozoic and Phanerozoic.

Taken together, the volcanogenic massive sulfides and the stratiform sedimentary sulfide ores probably account for nearly two-thirds of the world's total resources of the base metals. The remainder is mostly in hydrothermal environments associated with subvolcanic plutons such as the porphyry coppers.

The porphyry coppers are primarily products of Phanerozoic orogenic belts (*11*). Of the producing ore bodies, about 80 percent are Tertiary (70 m.y. or younger). Their distribution pattern in the circum-Pacific "ring of fire" and the Paleozoic Tethyan (Mediterranean) fold belts clearly relates them to consuming plate margins, but the precise details of this relation are not always clear. Some plutons apparently fill the throats of volcanoes. Others invade sediments well away from volcanic vents. A favorite site is near a continental margin where a subduction zone dips under the continent. This is the Andean type. Elsewhere, porphyry copper deposits are emplaced as much as 1500 km inland from the continental edge and even farther from any likely contemporaneous subducting trench (*12*).

Porphyry coppers (*13*), which seem to be part of island arc sequences, commonly carry important gold values. Molybdenite, up to values of about 0.06 percent, is characteristic of others, especially the Andean type and deposits such as Bingham, Utah, where the porphyry magma must have traveled through a substantial thickness of continental crust and may not be directly related to a trench. Molybdenite may be an index of contribution by continental crust at the site of magma generation or along its path to the surface. The porphyry coppers are hydrothermal systems related to plutons that crystallize from partial melts at least as complicated as second cycle. Some porphyry copper magmas have such a large continental contribution that they may be due to third-cycle anorogenic partial melting of continental crust rather than oceanic. The porphyry coppers are related to, but apparently do not grade into, porphyry molybdenum and tungsten and tin assemblages.

Silver

Most silver is produced as a by-product of copper, lead, or gold. Its temporal pattern most closely resembles that of lead. There are small silver credits in Archean copper and gold ores, but none of these could have been worked for silver alone. The same is true for Witwatersrand-type quartz-pebble conglomerate gold ores of the Lower Proterozoic.

Probably the oldest ore bodies mined primarily for silver are the unique bonanza deposits at Cobalt, Ontario. Here the silver is in veins with nickel and cobalt arsenides, cutting the Nipissing diabase which has been dated at 2175 m.y. Production reached 500 million ounces of silver, much of it at very high grades.

The oldest major ores in which silver is a substantial credit are the stratiform lead ores of the mid-Proterozoic, including the lead-silver bonanza at Broken Hill, New South Wales. The silver content of some of the Paleozoic stratiform lead ores of Europe contributed much of the world's silver prior to the discovery of the bonanza "epithermal" vein districts of western North and South America and Mexico. Shallow-vein ores from Latin America are still among the world's largest silver producers. Nearly all of these were formed during the last 70 m.y. The propensity for silver to follow sulfur added it to copper and lead as well as to gold ores in situations where hydrothermal circulation was powered by near-surface igneous activity.

The subvolcanic porphyry coppers and shallow "epithermal" veins, emplaced into emergent continental crust, are perhaps the most vulnerable major types for early removal by erosion, thus depleting their incidence in older rocks. However, this should also apply to associated volcanics. Yet similar volcanic suites are present throughout the geologic column, with only a few porphyry coppers before the orogenic belts of the Phanerozoic, from 500 m.y. onward.

Iron Ores

The concentration of world-class stratiform iron deposits in Lower Proterozoic rocks has long been recognized as one of the sharpest and most significant geochemical anomalies in earth history. The deposits are sediments of iron oxide interbedded with layers of impure chert (*14*), and the spectacular banded appearance in outcrop led to the name "banded iron-formations" (BIF's). The largest and most persistent of these, the Lake Superior type, commonly show shallow-water features such as stromatolites and ripple marks. They occupy intracratonic basins and continental shelves and are not generally associated with volcanics. They had peak development between about 2500 and 2000 m.y. ago and then precipitously declined at the mid-Proterozoic. Photosynthetic oxygen had long been generated in seawater by the biomass, but, owing to the abundance of buffers, the fugacity of oxygen had remained low. However, with continuing oxygen production, possibly coupled with a decrease in the volcanic supply of reductants as suggested by the decline of volcanogenic massive sulfides after 1800 m.y., the biomass finally overcame its buffers and free oxygen began to build up in the atmosphere (*15*).

There are few important BIF's younger than 1800 m.y., but many of ore grade (Algoma type) are present in Archean greenstone belts. These are generally smaller than the Early Proterozoic deposits, and they are commonly closely associated with volcanics. They extend back in geologic time to some of the earliest sediments known, the Isua series of Greenland, which gives dates older than 3700 m.y. (*16*). Isua BIF is not high grade (34 percent iron), but it qualifies as the oldest known ore deposit of any kind. It even shows carbonate and silicate-sulfide facies which contain a little copper sulfide. Thus the BIF's were a characteristic type of chemical sedimentation for nearly 2 billion years. Their demise was certainly a major event in earth's chemical history. It cannot be interpreted as an erosional artifact.

Sedimentary iron ores of the Phanerozoic are hematitic with variable amounts of shaly impurities and little cherty silica. These "ironstones" have been locally important sources of iron, as in the Minette ores of Europe and the Clinton ores of the southern United States, but they are far less significant quantitatively than the BIF's.

Igneous-related iron deposits are only locally important in world commerce, but they have growing scientific importance in the history of the earth. The magnetite ore body at Kiruna, Sweden, lies within a reddish, alkali-rich volcanic succession that is about 1500 m.y. old. A similar but much smaller ore body is present at Iron Mountain, Missouri, also in a red volcanic series associated with a red granite 1450 m.y. old. In both Kiruna and Iron Mountain there are minor sulfides, fluorine, and local concentrations of light rare earths, as well as about 1 percent phosphorus. Pilot Knob, which is near Iron Mountain, shows hematite-rich tuffaceous sediments interbedded with arkosic sandstones and felsic volcanics. Similar sediments are found at Hauki, near Kiruna, and at Baiyan Obo, People's Republic of China (*17*), where they contain commercial quantities of rare earth elements. The great new Olympic Dam copper-uranium-gold deposit near Roxby Downs Station in South Australia (*18*) bears many geochemical resemblances to this iron-ore group, since it is an iron ore itself, and it contains a rare earth credit plus phosphorus and fluorine.

All these deposits fall close to 1500 m.y. old, and all are related to highly oxidized, alkali-rich petrologic suites. These rock suites are widespread and possibly rift-controlled, as in mid-continent North America and central Australia (*19*). Along with the Late Proterozoic titanium-anorthosite association, they may have special significance with respect to anorogenic partial melting and differentiation beneath the supercontinent of the Proterozoic.

Gold

Of the total stock of the world's gold, probably about 30 percent is from modern and Tertiary placers that have been worked since the dawn of civilization. The bedrock source of this gold is commonly evident, as in the Tertiary gravels of California. If the placer gold in huge

Lower Proterozoic quartz-pebble conglomerates, such as the Witwatersrand, is assigned to Archean greenstone belts, it seems probable that more than 70 percent of the world's gold came from primary concentrations of Archean age.

Gold ore is present in veins in nearly every Archean greenstone belt, starting with the Barberton at about 3400 m.y. The most common host rock is basalt, but turbidites and chemical sediments also contain gold veins. The veins cut the beds in detail, but commonly they are strata-bound; that is, they favor a limited stratigraphic interval. The veins are commonly stubby and lenticular in strike and dip. Coarse white quartz is a common vein filling, with only small amounts of sulfide. Growth of the veins may have started early during deformation and metamorphism because some veins are themselves deformed, but, since the quartz locally includes breccia fragments of schist, growth must have continued after penetrative deformation was well advanced. Heat for activation of the hydrothermal system was apparently generated during metamorphism and deformation of the volcanic pile.

Phillips and Groves (*20*) have pointed out that there is a huge enrichment of gold over the base metals in the greenstone gold veins as compared to host rocks. In this respect the gold deposits contrast sharply with the volcanogenic massive sulfides, in which the copper/gold ratio is about the same in the ore as in the host rocks and gold is only a byproduct of base metal production. Fumarolic seawater solutions convectively circulating through the felsic volcanics evidently did not discriminate between the base metals and gold.

The gold-quartz veins in Phanerozoic turbidites and back-arc shales, such as the California Mother Lode, are generally associated with andesites and basalts along with ultramafics emplaced along major deep faults generated during obduction. The gold could be a direct contribution from the mantle into first-cycle basalts, and then, like Archean greenstone gold, it was increased to ore grade during deformation and metamorphism.

There is little evidence for the introduction of much new gold from the mantle into the crust from 2000 to 500 m.y. ago. There are only a few deposits of major significance, such as Tennant Creek, South Australia, in the upper Proterozoic. Gold in the Lower Proterozoic carbonate sulfide–facies BIF's (such as Homestake) has some characteristics in common with the Archean greenstone belts, including mafic volcanism, but the great quartz-pebble conglomerates are clearly reworked older gold. The Witwatersrand system contains the greatest ore accumulation of any kind in terms of monetary value. Progressive sedimentary reworking of fan systems on the north side of the basin probably accounts for the richness of the detrital ore shoots (*21*), as the basin tilted southward during its filling period from about 2700 to 2500 m.y.

There are at least 13 conglomerate-filled basins in the Lower Proterozoic, about half of which carry minable gold. In several, like Blind River, Ontario, detrital uraninite is more valuable than gold. The youngest of the gold-bearing conglomerates is Tarkwa, in Ghana, where the conglomerate lies on a surface composed of rocks dating from about 1950 m.y. ago. Tarkwa is also interesting because it has hematite in the matrix of the conglomerate but no detrital uraninite or pyrite. This was a transitional environment, sufficiently oxidizing to destroy uraninite and pyrite but not to dissolve the gold in a fluvial (nonsaline?) system. Gold is soluble in saline fluids under oxidizing conditions, and most of it probably was dispersed in seawater after the mid-Proterozoic oxygenation of the atmosphere. Pretorius (*21*) recently reemphasized that gold is not in the conglomerates after the first red beds, and detrital uraninite is no longer present as clasts after the decline of the BIF's.

Near-surface epithermal veins mined primarily for gold are locally important in some Tertiary volcanic fields such as in the western United States. Some of those have produced bonanza ore shoots of gold, or combined gold and silver, such as Goldfield and the Comstock. Most seem to be related to anorogenic volcanism, where thermal convection cells have recycled continental crustal gold.

Uranium

The distribution of uranium ores shows strong dependence on changes of oxidation potential in the environment. Redox fronts are spectacular as "roll-fronts" in plateau-type uranium deposits. The uranium was leached under oxidizing conditions from arkoses of interior basins and carried by ground water into beds where reductants such as sulfide or activated carbon were present. Precipitation as pitchblende or uraninite occurred at the reaction "front," while the transporting fluid passed on through (*22*).

The same general mechanism probably applies to the rich uraninite ores concentrated below mid-Proterozoic unconformities. Weathering of uranium-bearing rocks prior to oxygenation of the atmosphere provided detrital uraninite to conglomerates such as Witwatersrand and Blind River. Once the atmosphere contained free oxygen, however, this uranium largely went into solution and penetrated downward with ground water. In places where reducing conditions were encountered, rich ores could be precipitated in veins or breccias. Oxygenation of the atmosphere thus set the stage for the great ore bodies (1500 to 1600 m.y. ago) in places such as the Athabaska Basin and the Alligator River area, Australia. Even the uranium content of Olympic Dam may have been increased by this mechanism. From there on through the upper Proterozoic, uranium has been periodically on the move—dispersed and reconcentrated—as redox combinations change in weathering and sedimentation, right down to the Tertiary roll-fronts.

Molybdenum, Tungsten, and Tin

These metals are concentrated into ores primarily in igneous-related siliceous hydrothermal systems, including granites and their subvolcanic equivalent porphyries. Molybdenum is found in two kinds of porphyry systems: as a minor metal (0.05 percent) in the porphyry coppers and at higher concentrations (up to 0.3 percent), with minor copper and tungsten, in siliceous porphyry molybdenum deposits such as Climax, Colorado. The two types of ore bodies do not appear to be fully intergradational. Moreover, the molybdenum prophyries are in tectonic situations that suggest third-cycle magmas generated more from continental crust than from descending oceanic slabs. In the western United States, for example, they are found (i) along with bimodal volcanics where sprays from the Rio Grande Rift system cross the Colorado Mineral Belt and (ii) where there is crustal imbrication related to accretion of the western part of North America. Heating of the lower continental crust may be the critical factor. Porphyry molybdenum deposits are like porphyry coppers in that they have gangue and alteration assemblages, including sulfates, which suggest moderately high oxidation states (*23*).

Wolframite tungsten ores and cassiterite tin ores are generally in veins representing the siliceous residues of granitic rocks that are sulfur-poor and fluorine-rich relative to the porphyry coppers. Significantly, these magmas were also generated mostly in Phanerozoic belts involving imbrication or thickening of continental crust, with depression into higher temperature zones. At such sites when granitic partial melts could be generated, collector mechanisms for tin and tungsten might be enhanced if there were carbon or other reductants in the melted rock. Third-cycle magmas generated in these ways are more likely to result in S-type (partial melts of sediments) or ilmenite granites (*24*) whose subsequent differentiation to siliceous, fluorine-rich residues further concentrated the tin and tungsten. Once the "collector mechanism" at the point of magma generation has operated preferentially for tungsten and tin, these elements are destined to appear in ores that are the final differentiation products of these magmas, such as wolframite veins in southeastern China and the tin veins of Cornwall.

Large commercial deposits of molybdenum, as well as tungsten and tin, are very strongly biased in age toward the Phanerozoic. The largest molybdenum deposits are less than 50 m.y. old, but some world-class tin deposits go back to the mid-Paleozoic (350 m.y.). Tungsten peaks between the two, largely because of the wolframite with Cretaceous granites in southeastern China. Tin and tungsten granites may have been emplaced somewhat deeper than the molybdenum porphyries, but all were evidently close enough to the surface to produce strong vertical zoning. As in the porphyry coppers, tin and tungsten granites are in tectonically vulnerable positions so that removal of older deposits by erosion could account for some of their preference for the Phanerozoic. However, porphyry ore-forming systems, to produce copper through molybdenum and tungsten to tin, must have a wide range of redox level at the sites of magma generation. Probably that range was most effectively developed in the Phanerozoic, when it was also coupled with tectonically vigorous continental plate collisions and imbrications to generate magmas by partial melting of continental as well as ocean crust.

Conclusions

Archean greenstone belts, ranging from about 3600 to 2500 m.y. in age, are some of the richest repositories of ore in earth history. The high quality of chromite ore at Selukwe makes Archean podiform chromite ore an attractive target. Most of the world's gold probably started its crustal migration in Archean greenstone belts. BIF ores are also widespread, but Kambalda-type high-grade nickel sulfide ores and large volcanogenic massive sulfides are concentrated in the younger Archean belts from about 2900 m.y. to the end of the Archean. The nickel is mainly in western Australia, and most of the copper and zinc is in Canada where there are higher proportions of felsic rocks in the visible parts of the successions. The paucity of lead in the Archean base metal deposits may be related to the rather low potassium content of the Archean greenstone volcanic suites. Nickel sulfide ores in ultramafics are dependent on the localization of sulfur; small amounts of nickel are almost ubiquitous in the silicates.

The tectonic transition from Archean to Proterozoic began with the oldest preserved large basins, about 3000 m.y. ago in Southern Africa and 2500 m.y. ago elsewhere. In Africa, a succession of these basins culminated in the quartz-pebble conglomerate which contains the world's largest ore deposit, the Witwatersrand gold fields. Interestingly, other epicontinental basins were filled with cherty iron deposits (BIF's) at about the same average rate of sedimentation.

A number of major changes converge at the mid-Proterozoic, centering at about 1800 m.y. Most of these relate to the high rate of increase of free oxygen in the atmosphere and the availability of carbonaceous reducing sinks in basins of restricted circulation. Prokaryote photosynthesis, which had been precipitating the world's largest BIF's, seems to have outstripped its buffering supply of chemical reductants.

There were many responses to the increase in oxygenation of the atmosphere. Iron was fixed on the weathering outcrop. Sulfate became widespread in seawater and even in evaporites. Hence, where organic debris accumulated to make locally reducing bottoms, sulfides could be deposited. If base metals were available, sedimentary sulfide ore bodies were formed. Detrital pyrite and uraninite, although abundant in earlier gold-bearing pebble conglomerates, are not present later than Tarkwa in Ghana (1950 m.y. old), probably because gold is slowly soluble in saline solutions under oxidizing conditions.

The copper deposits at Udokan, U.S.S.R., and Outokumpu, Finland, appear to be the oldest of the large stratiform sulfide ore bodies, but the next great stratiform cycle, starting around 1700 m.y., generated much of the world's lead in a period of less than 200 m.y. The controls on the availability or selective precipitation, or both, of copper versus lead in these and later basins are not clear. Implications are somewhat stronger for differences in source rather than controls at the sites of deposition. It may be that the great lead deposits are the product of the extraction of lead from incipient potassium-rich partial melts under the Proterozoic supercontinent.

Special igneous-related ore types, such as the anorthositic ilmenite-titanium ores and the iron oxide–rich ores associated with alkalic volcanics, appear to have been especially prevalent just after the mid-Proterozoic, a little younger than that first big surge of lead. Potassium-rich magmas could have been generated by very small degrees of partial melting, owing to the thermal insulation that a large thick stable continent would provide. Heat dissipation during the Late Proterozoic may have been mainly by rifts and mobile belts, following the last major episode of Archean-style greenstone volcanism and deformation which had provided the Archean-style volcanogenic massive sulfide deposits in Wisconsin and Arizona and in the Churchill province of Canada. It is difficult to quantify, but possibly the temporary demise of this sulfur-rich volcanism at the mid-Proterozoic triggered the collapse of the buffering system which had maintained low concentrations of atmospheric oxygen.

Finally, the tentative plate motions of the late Proterozoic evolved into the great Phanerozoic orogenic belts that produced the most variegated retinue of ore deposits of any geologic period. Basins in the Phanerozoic were smaller than in the Proterozoic, but the types of deposits were broadly similar; local reduction sinks were provided by carbon accumulations. Back-arc basins accumulated gold-rich black shales in turbidites, whose deformation and metamorphism subsequently produced gold-quartz veins such as the Mother Lode in California.

Volcanogenic massive sulfides came back in style, related to volcanics at accreting as well as consuming plate margins. On the average, Phanerozoic massive sulfides are smaller than Archean massive sulfides, and the Cyprus type with ophiolites appears to be new. Lead is added to copper and zinc in the ores at consuming plate margins, such as the Kuroko of Japan.

The porphyry coppers and allied stockworks and veins of molybdenum, tin, and tungsten rose from incipient to major proportions during the Phanerozoic, especially in the last 80 m.y. These metals span a wide range of redox requirements for solubility in the magma at the site of magma generation. This range was probably provided by the variation in the carbon content of continental crust available for partial melting. Through its oxygen-carbon energy storage cell, the biomass has influenced the patterns of nearly all the ore metals, except perhaps those of chromium, nickel, and titanium.

References and Notes

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25. This article incorporates important suggestions made by a reviewer. V. B. Meyer assisted with editorial work and prepared the manuscript. I am grateful to both, but especially to Editor P. H. Abelson for his interest over the years in resource appraisal, stimulating papers, wise editorials, and compilations on energy and minerals which awakened the interest of a wider constituency than geologists ordinarily reach.

Genetic Basis for Species Vulnerability in the Cheetah

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Over 1000 animal species, many of them mammalian, have been recognized by the Convention of International Trade in Endangered Species as being threatened by extinction (*1*). Although 1000 seems a large number, it probably represents a minor part of a larger process (*2*, *3*). Myers (*2*) estimated that, of the 5 to 10 million living biological species, as many as 1 million probably will become extinct by the turn of the century. At the present accelerating rate of extinction, this translates to losing one species every hour. Many large mammals already have become extinct in the wild and survive today only under managed breeding programs in zoological parks and wildlife preserves (*4*). The accelerated rate of habitat destruction has led to the prospect that in the next century virtually all exotic wildlife will be managed in captive breeding programs. Several programs have been successful (most notably those involving Père David's deer, the Mongolian wild horse, and the European bison), but other species (such as clouded leopards, penguins, and condors) have done very poorly under captive propagation conditions (*4*). The reasons for success or failure in these programs are obscure, since scientists and curators have almost none of the necessary background information for species that are threatened or rare (*2*).

There are 37 species in the cat family (Felidae), and all except the domestic cat are considered threatened or endangered (*1*). The cheetah (*Acinonyx jubatus*) is the single surviving species of the genus *Acinonyx* and is considered by most taxonomists to be markedly divergent in both anatomy and behavior from the other genera in the Felidae (*5*–*7*). Cheetahs, the world's swiftest sprinters, have a number of cursorial adaptations that make high-speed pursuit (up to 112 km/hour) possible (*5*): long, slender legs; enlarged respiratory, cardiovascular, and adrenal capacities; specialized muscles for high acceleration; and semiretractile claws (*5*, *6*). Because of its swift and elusive character, demographic estimates of wild cheetahs vary considerably (from 1,500 to 25,000 animals) (*8*–*11*). Most animals are restricted to two remaining wild populations in southern and eastern Africa, where the population density is less than one animal per 6 km^2 (*9*). This low density can be partially explained by the cheetah's solitary nature, for, unlike the lion, the cheetah usually avoids family groups (*8*, *11*). In addition, cheetah cubs appear to suffer severe mortality (estimated at as high as 70 percent) due to disease susceptibility, maternal neglect, and insufficient defense against predators (*12*).

In 1971 the National Zoological Gardens of South Africa initiated a comprehensive program for the propagation of cheetahs in captivity (*13*). In 1981 40 semen samples from 18 cheetahs were collected, examined, and compared to the semen of domestic cats (*14*). Spermatozoal concentrations in ejaculates were ten times less in cheetahs than in domes-

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