Metallogeny—the search for a rationale behind space-time selectivity of ore deposit formation

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Ore deposits, localized natural concentrations of some metals way above their average crustal abundance, have been forming almost from the beginning of earth's history (~3.8 Ga) to the present day. Global database reflects their strikingly non-uniform distribution patterns which can be region-specific, time-specific and/or metal-specific. Attempts to rationalize such spatial/temporal/compositional selectivity in terms of the broader processes of crustal evolution have been only partially successful so far. However, such efforts have revealed many hitherto unsuspected relationships between mineralization and seemingly unrelated geologic phenomena. A complete understanding—of reasons why ore deposits occur *when* and *where* they do—must await fuller recognition of such nexus.

THERE is a standing joke among exploration geoscientists that ore geneticists never fail to come up with an erudite explanation about *how, when* and *why* a particular deposit was formed at a particular place—but only long after the deposit had been actually discovered; often through routine hard work of field-weary geoscientists and sometimes by sheer chance!

One reason why such pedagogues are indulgently suffered is that they are really trying hard to find a method in the madness of Nature; to understand why an ore deposit is where-it-is, was formed when-it-was-formed, and whether there is any discernible, regionally or globally unifying pattern in their space-time distribution that can be explained in the light of known and emerging facts of the earth's evolutionary history. This in essence is what metallogeny is all about.

What is an ore deposit? It is essentially a segment of the earth's crust with a strong positive chemical anomaly in respect of certain element(s) whose *average crustal abundance* (called the Clarke value) is very much lower. Every deposit, large or small, is thus a reminder that something very special must have happened there, so that elements with Clarke values in ppm/ppb range have been concentrated in several million tons within a small volume of rock. The degree of natural enrichment required to be labelled as an ore 'deposit'—even though dependent on technoeconomic factors—is so widely different (Table 1) as to imply that it is either *more difficult*, or *more time-consuming*, or *both*, for Nature to produce deposits of some metals (e.g. Hg, As, Sb), compared to those of some others (e.g. Fe, Cr, Al). A deposit may be a very rich bonanza with a sharp, discrete boundary, or an invisible lean dispersion whose outline is delineated by an arbitrary assay contour cut-off, decided primarily by cost–benefit calculations.

Two endmember earth processes are responsible for diverse genetic types of deposits: *endogenous*, driven by the earth's internal heat engine, and *exogenous*, operated by solar energy. However a large majority of ore deposits are really 'hybrid' products of joint enterprise of the two processes. The same process can give rise to deposits of different metals and different genetic processes can form deposits of the same metal. Quite often, formation of an ore deposit is a multistage operation creating, first, a lean 'protore' and subsequently a further-enriched, smaller and richer orebody(ies).

Interestingly, except Al and Fe (and Mn), metals eagerly sought for are not at all essential for forming the ordinary rocks in the crust. These metals are, so to say, unwelcome stragglers who have to be either grudgingly accommodated by the rock-forming silicate minerals in their lattice or disposed of somehow, somewhere. Seen in that light, formations of ore deposits may be looked upon as Nature's waste disposal arrangement—through its own sewers into its

Table 1.

Element	Clarke (ppm)	'Cut-off grade* (ppm)	Required enrichment factor
Al	81,300	300,000	4
Fe	50,000	280,000	6
P	1,050	100,000	95
Cu	55	10,000	160
Nb	20	3,400	170
Ni	75	1,500	188
Mn	950	350,000	350
Pt	0.01	4	400
U	1.8	1,000	500
Zn	70	40,000	600
Mo	1.5	1,300	867
W	1.5	1,400	933
Au	0.004	6	1500
Pb	13	40,000	3000
Cr	100	300,000	3000
Sn	2	10,000	5000
Ag	0.07	500	7143
Hg	0.08	3,000	37,500
Sb	0.2	10,000	50,000

**Variable technoeconomic parameter.*

own dumping grounds. These sewers (channelways) and dumping grounds are, for obvious reasons, the focal points of interest for ore geneticists.

To come back to our central theme, we need to demonstrate:
that exclusivity in *spatial* and *temporal* distribution patterns of ore deposits is recognizable;
that such patterns are *real*, and not artefacts—due to inherent sampling error and/or episodic nature of the events, and;
that certain features of the evolutionary process of the 'whole-earth' system relate, causatively, to such patterns.

Ores in space

Spatial distribution patterns are most easily recognizable. Inhomogeneity of distribution of mineral deposits on the globe has shaped the course of history to a great extent, leading to the Industrial Revolution, the North–South divide, colonialism, wars and other forms of aggressive geopolitics. 'Metallogenic provinces' repeatedly stamped with the hallmark of *a* specific metal have been known for more than a hundred years. Such provinces may be as large as the southern tip of Africa where two-thirds of the world's known chromite resources were formed over 1000 Ma, or as small as the climax mine in Colorado where an area of about two km^2 supplied 80% of the world's total requirement of molybdenum for several decades. Site preference for mineral deposits is also manifest in numerous ore–lineament associations, such as the Singhbhum copper belt, where a large number of deposits occur along deep crustal flaws extending for hundreds of kilometres. While the most compelling evidence comes from discovery of more than four hundred 'live' ore-forming systems along present-day midoceanic ridges and rift regions like the Red Sea, close matching of mineral belts in reassembled continents of present (Figure 1) and past (Figure 2) configuration tells us that such site preference had been a persistent feature since antiquity.

One must emphasize that these preferred sites are not just geographical ones. They represent different kinds of thermotectonic, sedimentational and/or climatic regimes prevalent at the time of ore formation—each having its own evolutionary history.

It has become increasingly clear now that the plate tectonic paradigm provides a satisfactory framework within which such spatial exclusivity of many ore deposits can be rationalized. Sites of mineralization taking place today *on* or *within* the ocean floor several kilometres below sea level, are now accessible with research submersibles like the *Alvin* for collection of materials from, and observations of processes operating, there. From critical examination of modern/recent mineralization sites at (a) convergent plate boundaries, with their compressional forearc and extensional back-arc environments, (b) seafloor spreading centres, (c) oceanic ridges and continental rifts in early and advanced stages of rifting, and (d) collisional tectonic regimes of recent/subrecent times, the rationale for site preference of mineralization has come into much sharper focus. More importantly, the relationship observed between the preferred tectonic sites and the style of mineralizations now taking place therein can be extrapolated to the remote past on the basis of 'frozen' diagnostic records of such environments in ancient rocks. Details, however much interesting to earth

Figure 1. 'Across-ocean' matching of positions of tin belts in reassembled present-day contents. Dark areas within belt indicate rich deposits (From ref. 8).

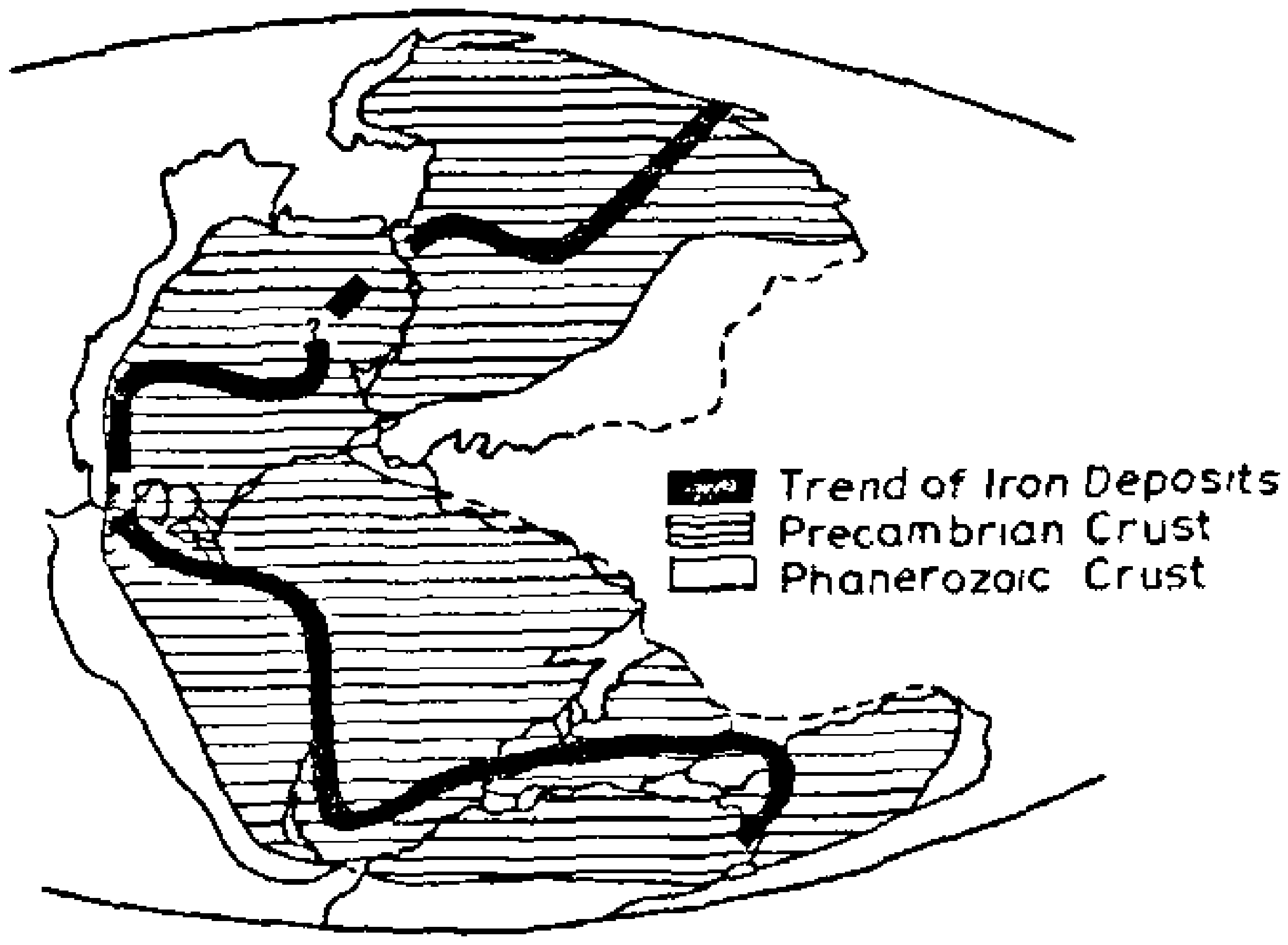

Figure 2. Early Proterozoic Banded Iron Formation displaying a well-defined global trend on a reconstruction of Pangaea (From ref. 9).

scientists, may be skipped for the general readers and it would suffice to say that site preference for mineral deposit formation is *real*, is *demonstrable*, and is *explainable*, at least in a broad way, in terms of crustal evolutionary processes.

Ores in time

Not so is the case with the *temporal distribution pattern* of ore deposits.

Conventionally, such patterns are sought to be recognized by plotting age-vs-tonnage proportion diagrams where relative contributions from different genetic types for each metal can also be taken into account (Figure 3). Careful examination of this diagram reveals the following salient features:

(a) Inhomogeneous *temporal* distribution of both metal *deposits* and ore-forming *processes*—Sn, W and Mo deposits virtually all confined to the last 1000 m.y.; Ti ores within 2000–1000 m.y. time span; Pb-ores practically all within the last 2000 m.y. and none before the earth was 1000 m.y. old. Similarly, some distinctive ore-forming processes, such as 'porphyry type' Cu (± Zn ± Au), Sn, W and Mo skarns and the 'Mississippi valley' type of Pb-Zn (± Ag), all belong to the Phanerozoic, i.e. the last 600 m.y. period.

(b) Well-defined abundance maxima in respect of some metals such as the strongly bimodal distribution of gold, the unique period of prolific Banded Iron Formation (BIF), etc.

(c) Increasing diversity of ore forming processes culminating in maximum proliferation during the Phanerozoic—as is evident from the crowded population in the extreme right hand column of Figure 3.

(d) Overall paucity of both *deposits* and *types* during the first 1000 m.y. of the earth's history. There are also other lean periods of mineralization.

Now, if we are able to match these features—causatively, and point-to-point—with coeval, broader geological phenomena, we may possibly be in a position to answer the query: why were ore deposits formed when-they-were-formed? For instance, there is near-simultaneous disappearance of transported uraninite (UO_2) placers in five continents at around 2.3 Ga [Uraninite can survive weathering only if atmospheric oxygen level is below 1% of the present atmosphere level (PAL)], indicating an increase to >1% PAL in the atmosphere O_2 level at that point of time.

There are however two major reservations in accepting such projection as real; therefore the generalizations that emerge from the temporal spectrum are also suspect.

First, the age distribution patterns are strongly influenced by a few giant deposits like the Witwatersrand gold field in South Africa or the Krivoi Rog iron ore deposit in Ukraine which dominate the total reserve. However the saving grace is that geologic time spans accommodating such superlarge deposits also invariably contain a large number of smaller deposits. So, even if the giant deposits are ignored, the distribution 'peaks' would still be there, though in a subdued manner.

Second (a much more serious objection first voiced most articulately by Veizer and his associates[1,2]), ore deposits once formed are not hermetically sealed in rock-time capsules for eternity; these are all subject to recycling, of both closed-system, cannibalistic (erosional) type and open-system, predaceous (subductional) type, the *probability* and the *rate* of recycling depending primarily on where these deposits were formed and/or rested. Therefore mineral deposits cannot really be inventoried like accumulated stock of articles bearing manufacturing-date labels and kept in pilfer-proof godowns. Rather they resemble 'living' systems with birth–death cycles, a situation which demographers treat quantitatively through the formalism of population dynamics.

Let us recall, briefly, that for quantitative treatment of a population with birth–death cycles, the two essential parameters are the *population size* (A_0) and its *recycling rate* (b) that relates to the population size normalized to one. The relationships are shown in Figure 4.

The cumulative curve, depicting the internal age distribution within the population, displays an exponential or power law relationship and also defines the population's half-life (τ_{50}), mean age (τ_{mean}) and life expectancy (τ_{max}). Obviously, the faster the recycling rate, the steeper the slope of the cumulative curve, the shorter are τ_{50}, τ_{mean} and τ_{max}. When the combined mortality of all age groups during a time interval equals the number of births during the same interval, the population attains a steady state; the slope of the curve remains the same while propagating into the future.

Natural systems obtain three fundamental types of internal age distribution pattern (Figure 5). The ideal type (type I), now a straight line on a semi-log plot; the type II pattern, reflecting high infant mortality rate with chances of survival increasing with attainment of puberty, is typical of human population in underdeveloped countries; and the type III pattern, representing population with low infant mortality rate, as in the developed countries. In a prolonged time frame of reference it is common to have partial intervals with recycling rates slower/faster than the average rate.

Strictly speaking, the type II pattern can have two alternative interpretations: (a) a high infant mortality or (b) a constant mortality rate throughout the age groups but excessive birth rate during the latest history. Likewise, the type III relation may be a consequence of either (a) higher mortality rate of older age group or (b) constant mortality rate throughout the groups but a population explosion during the early evolutionary

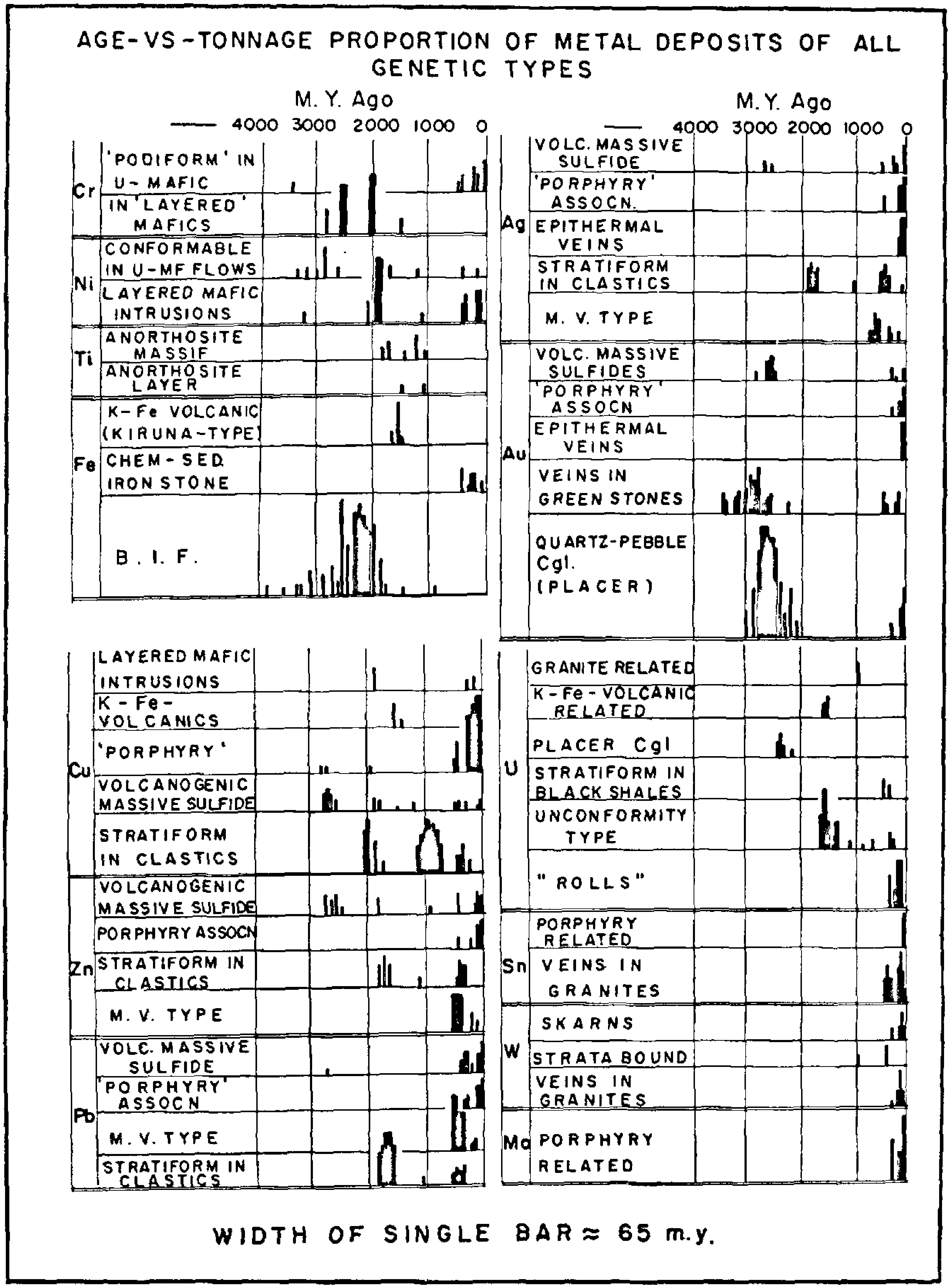

Figure 3. Age-vs-tonnage proportion diagram for selected metallic ore deposits formed by diverse genetic process. The sum of the heights of all genetic types for a metal equals its total known global reserve (From ref. 10).

QUANTITATIVE PARAMETERS

- POPULATION SIZE (A) NORMALIZED to 1 (100%) population
- $A_{t_*} = A_0 e^{-Kt_*}$ .... (1)

[A_{t_*} = Cum-fraction of the surviving population older than t_*
$A_0 = 1$
t_* = Age (not time)
K = rate const. for recyling] (Recycling = Natality/mortality)
$b_T = 1 - e^{-KT}$ .... (2)
b_T = recycling proportionality const;
T = Time Resolution
τ_{50} = 'Half-life'
τ_{max} = maximal life expectancy (at 95% conf. level)

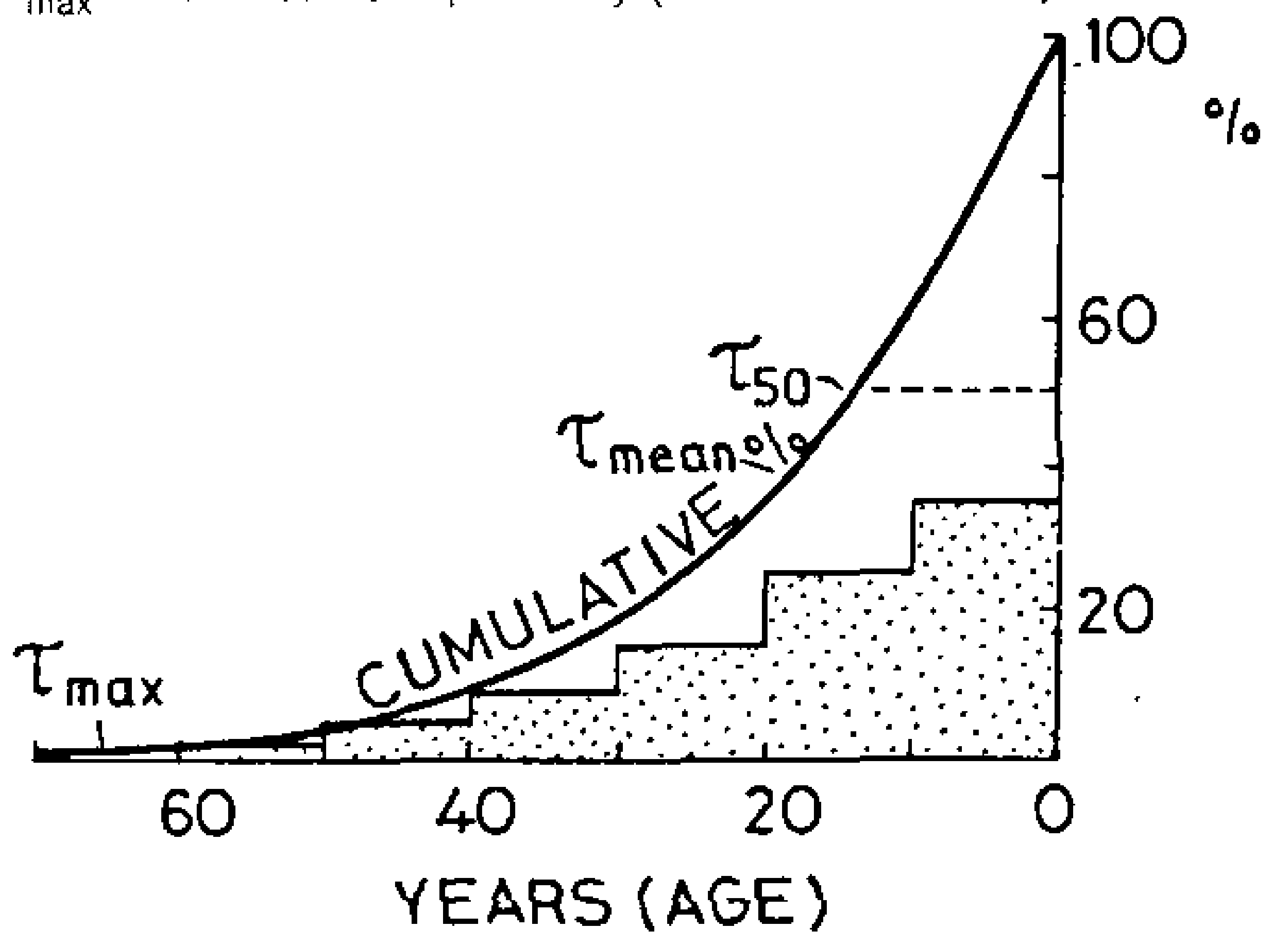

Figure 4. Ideal internal age distribution pattern of a hypothetical 'living' population (From ref. 1).

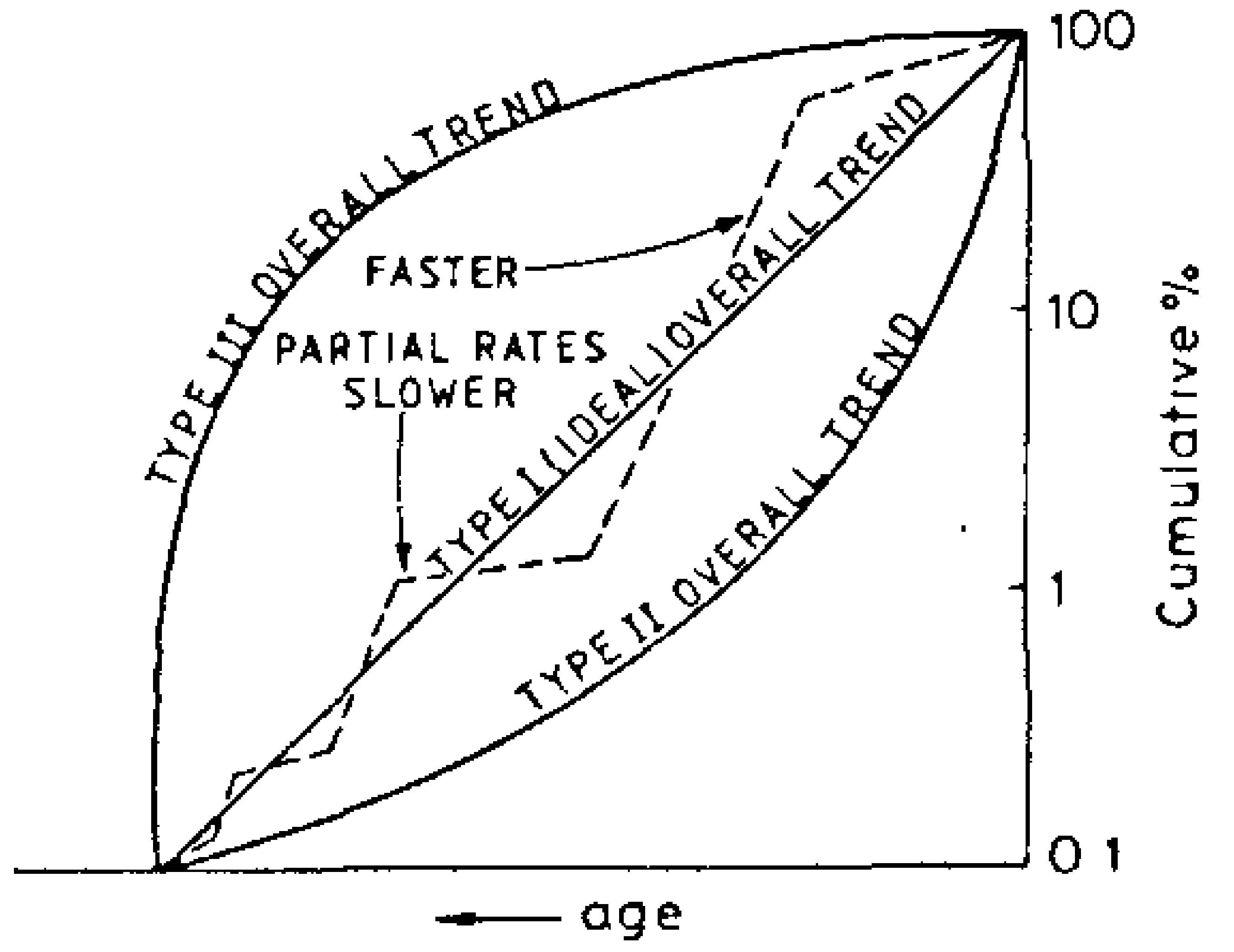

Figure 5. Cumulative age distribution pattern for three commonest types of survivorship trends in a 'living' population (From ref. 1).

stage. Additional information is required to choose the correct alternative.

Is this formalism of demographers' population dynamics relevant and applicable to ore deposits? From the global database, the cumulative age distribution patterns for different metals can be constructed (Figure 6).

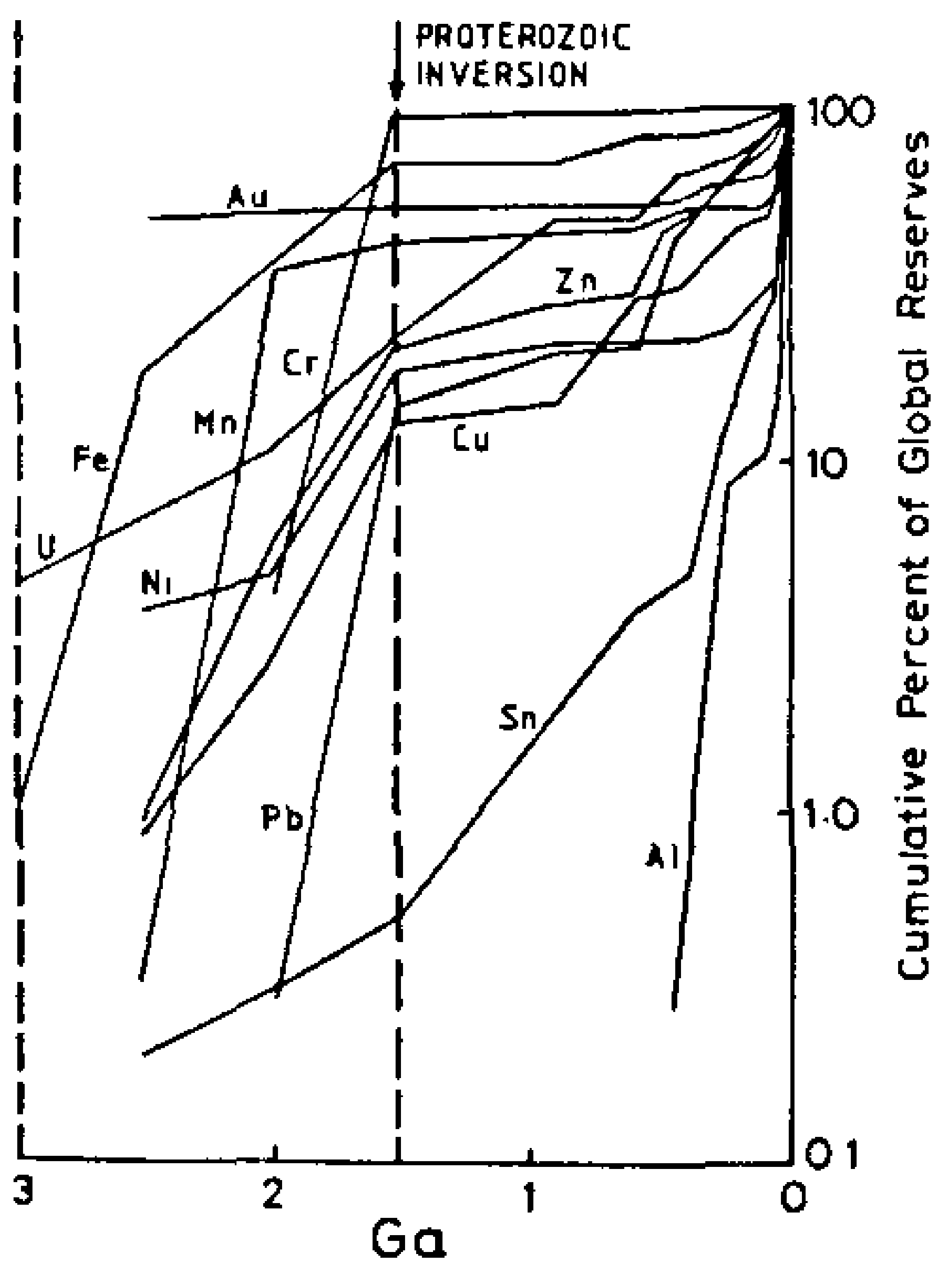

Figure 6. Present-day cumulative age distribution pattern for known global reserves of selected metallic ores (From ref. 1).

Here we notice the following:

- *An overall pattern* indicating a two-stage evolutionary history for virtually each metal, with a break at ≈1.75±0.25 Ga, the so-called Proterozoic Inversion (PI)[1]
- *In the post-inversion section*
  Array of curves with progressively diminishing slopes from Al to Cr
  All curves concave upwards, conforming to type II preservation probability
- *In the pre-inversion section*
  Steep plunges in accumulated reserves conforming to type III pattern reflecting, as stated earlier, either an increased rate of destruction *or* a constant destruction rate but excessive growth during this early stage of terrestrial evolution. The fact that the continental crust attained its near-present-day steady-state areal extent at ≈1.75 Ga, following an enhanced growth rate during late Archaean early Proterozoic time, points to the second alternative.
- *The two sections taken together*, then, imply *high growth rates* at the early stage and *differential recycling rates* after the Proterozoic Inversion for most metals.

It is interesting to note that the higher the recycling rate, the more advanced the obliteration of early growth-stage memory from the record, and the more complete is the type III → type II (or I) transformation. For instance the recycling rate for Al, which forms bauxite deposits on the land surface, works out to be very fast with a half-life ≈40 Ma. Therefore some

45 ± 5 half-lives have elapsed since the Proterozoic Inversion and the record of early bauxite deposits is all but erased from the 'ledger'. In contrast, the recycling rate for Cr (which forms deposits deep within the crust in layered igneous complexes and 'Alpine type' intrusives) is near-zero during the post-inversion period and their earliest records are preserved almost in toto.

One is therefore justified in accepting that the formalism of population dynamics holds good for the inventory of metal deposit population as well, and that the slopes of the preserved age distributions patterns are a reflection of their later stage recycling—at different rates for different metals. It follows, then, that in order to obtain the 'true' undistorted temporal spectrum of metal deposit distribution, we must filter off and 'see through' the effects of late recycling. This can be done[2] by 'deconvolution' or 'unrecycling', *at a* geologically realistic *invariant recycling rate,* where the deconvoluted reserves relate to all existing accumulations (cumulative percentage) present at a given point of time. The *net rate* of generation or destruction for a given time interval is a tangent to the slope of the deconvoluted reserve, with a positive or a negative slope respectively.

Figure 7 shows the *net* rate of generation (positive derivative of d(%)/d*t*) of several metals (by some selected processes) per 10^7 yr. Here the absence of a peak indicates a *net* generation ≤0, any actual generation having been offset or overweighed by coeval destruction of some older deposits (negative derivatives plotting below the zero axis are omitted). Such a projection—and not the simplistic, age-vs-tonnage proportion diagram—provides the true picture of periods of net positive (or negative) growth of deposits of specific metals. The figure demonstrates that temporal exclusivity of ore deposit formation is indeed real and, as brought out in the upper part of the diagram, its relationship with well-known major features of global tectonic evolution is discernible, at least broadly: The earliest 'Greenstone belt' stage accommodated gold, 'Algoma type' iron ore and massive basemetal sulphide deposits; 'Superior-type' iron ores, palaeoplacer Au and U and Mn deposits proliferated during the next 'Cratonization stage'; the 'Rifting stage' was characterized by ores of Cr, Ni, Cu, etc.; and so on. However, the rationale for such temporal selectivity still remains largely speculative.

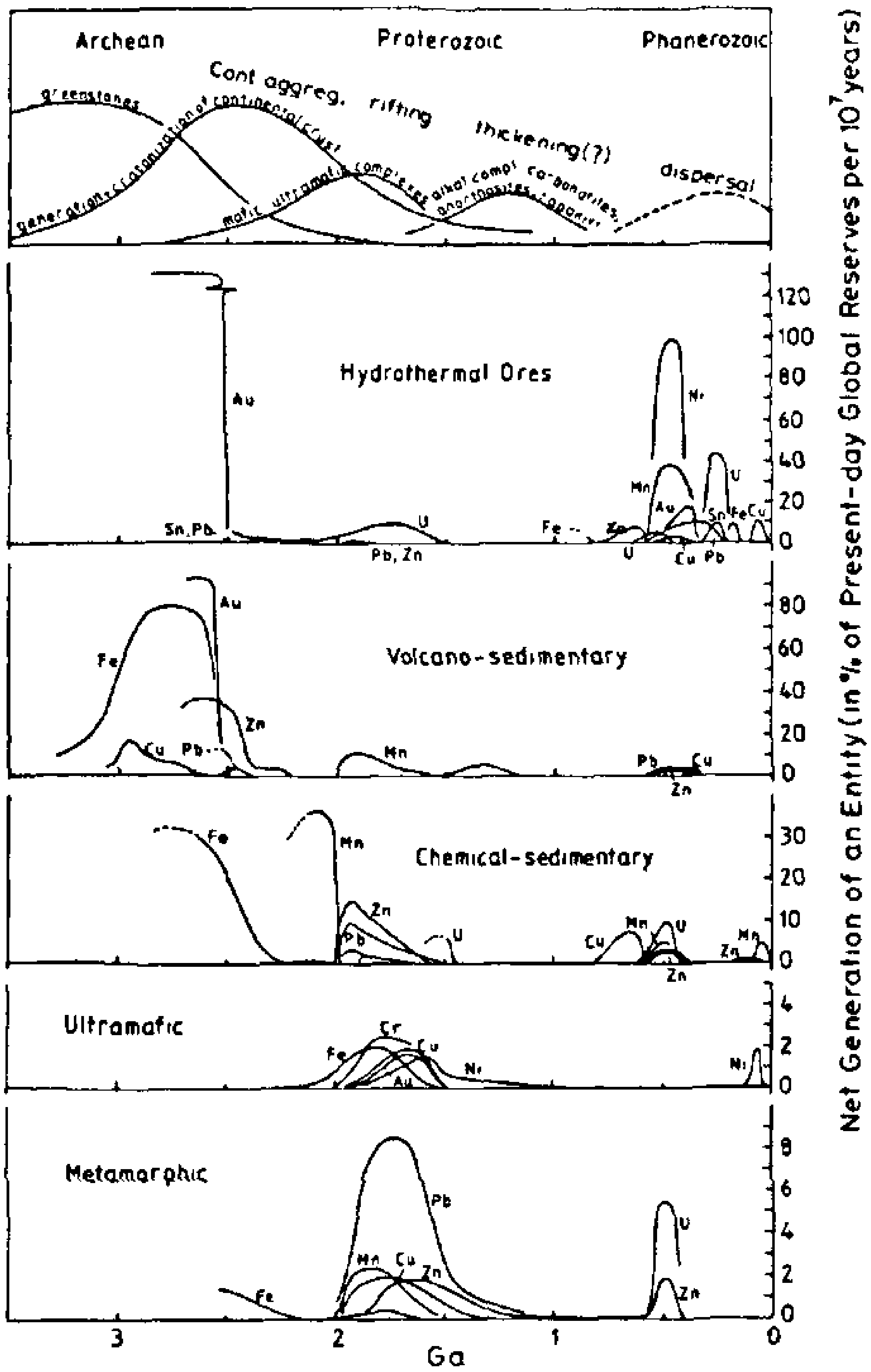

Figure 7. Summary of 'deconvoluted' pattern of mineralization of selected ores, as they relate to geologic evolution of the crust through time (From ref. 1).

The intricate nexus

It is so because the story is still incomplete. So far we have tried to relate mineralization with only the broader tectonic evolution of the crust which is basically a response to changes in the *rate, mechanism* and *sites* of internal heat generation and its dissipations over geologic time. While *endogenous* ore formation is primarily dependent on mantle-driven processes and is therefore expected to relate to the time when, and the sites where, these processes had been operative, the *exogenous* and the *'hybrid'* types—more prolific and diverse—could conceivably relate also to favourable climate and (palaeo) latitude (bauxite), to suitable geomorphic conditions (placers), to periods of special atmospheric composition (U-conglomerate), to 'ocean anoxic events' and many other parameters with which new, hitherto-unsuspected relationships are being discovered. For instance, the Phanerozoic oolitic iron ores seem to follow the greenhouse phases of supercycles[3,4] quite closely: the six major periods of hydrocarbon source-bed formation seem to synchronize with the times of high stands of sea level[5,6]. The crux of the problem, however, is: are these relationships *causal*; or are these *casual* coincidence, and we are perpetrating the classic '*post hoc, ergo propter hoc*' (after this, therefore because of this) fallacy?

Earth history had been a composite essay of processes of unidirectional (increasing or decreasing) *trends*, sinusoidal *cycles* and '*once-only' occurrences*[7]. Processes whose amplitude had decreased through time include endogenic heat production, meteorite encounter, surface temperature, CO_2 level; processes whose intensity has increased as a function of time are O_2 level in the atmosphere $^{87}Sr/^{86}Sr$ in seawater, continental growth, solar luminosity received, enzyme efficiency, organic diversity and complexity, etc. Sinusoidally recurring events include continental 'fragmentation–dispersal–assembly–stasis–fragmentation' cycles, greenhouse–ice-house cycles, ocean anoxic event cycles, marine transgression-regression cycles, biotic crisis–boom cycles[6], etc., many of which have the *same* and *synchronized* periodicity suggesting a common cause. Events of non-recurring singularity are represented, for example, by the Banded Iron Formation, komatiites and boninites—all 'one-time only' rock types in the crust. As most of these processes/events are being quantified and dated with greater precision and refinement, we are just beginning to realize that cause–effect relationship, between mineralization on the one hand and these *trends, cycles* and *non-recurring events* on the other, obtains in a much more complex manner than was initially guessed; and that the 'site-where' and the 'time-when' are not necessarily independent, unrelated variables.

Space does not permit discussion of all such relationships 'unearthed' so far. A case worth mentioning is the spatial and temporal changes in the style of exogenous U-mineralization that relate so delicately to the O_2 level in the atmosphere as to suggest that these deposits could possibly be used to constrain the atmospheric O_2 level through time (Figure 8). Detailed examination of two specific stages of a Wilson cycle—the supercontinental build-up and the continental break-up—serves to illustrate how several seemingly unrelated phenomena are, in fact, intricately intertwined with one another and also with some specific types of mineralization.

Building-up of supercontinents (Pangaea) every time had three major first-order consequences—(a) shrunken land area and increased ocean-floor surface, (b) high heat flow through thickened continental 'heat lens' and (c) decrease in number and length of midoceanic ridges. The first would lead to marine regression with coeval biotic crises[6]. The second caused increased partial melting of continental lithosphere which, in its turn, produced anorogenic granites *with related Sn-W-base metal deposits* and also spewed out plateau basalt and high volcanic ash into the atmosphere. The third was responsible for lower mean oceanic temperature, low CO_2 release and strong ocean current; these, aided by high volcanic ash in the atmosphere, ushered in icehouse climate (Figure 9). Rifting and dispersal of continents (Figure 10) similarly brought forth three major first-order phenomena which, in their turn, were harbingers of marine transgression, greenhouse climate and ocean anoxic events with expanded O_2-minimum zones in the ocean—features that would offer favourable habitats/situations for a variety of mineral deposits.

Conclusions

We conclude that spatial and temporal selectivity of ore deposit formation is an established 'fact of life' of our

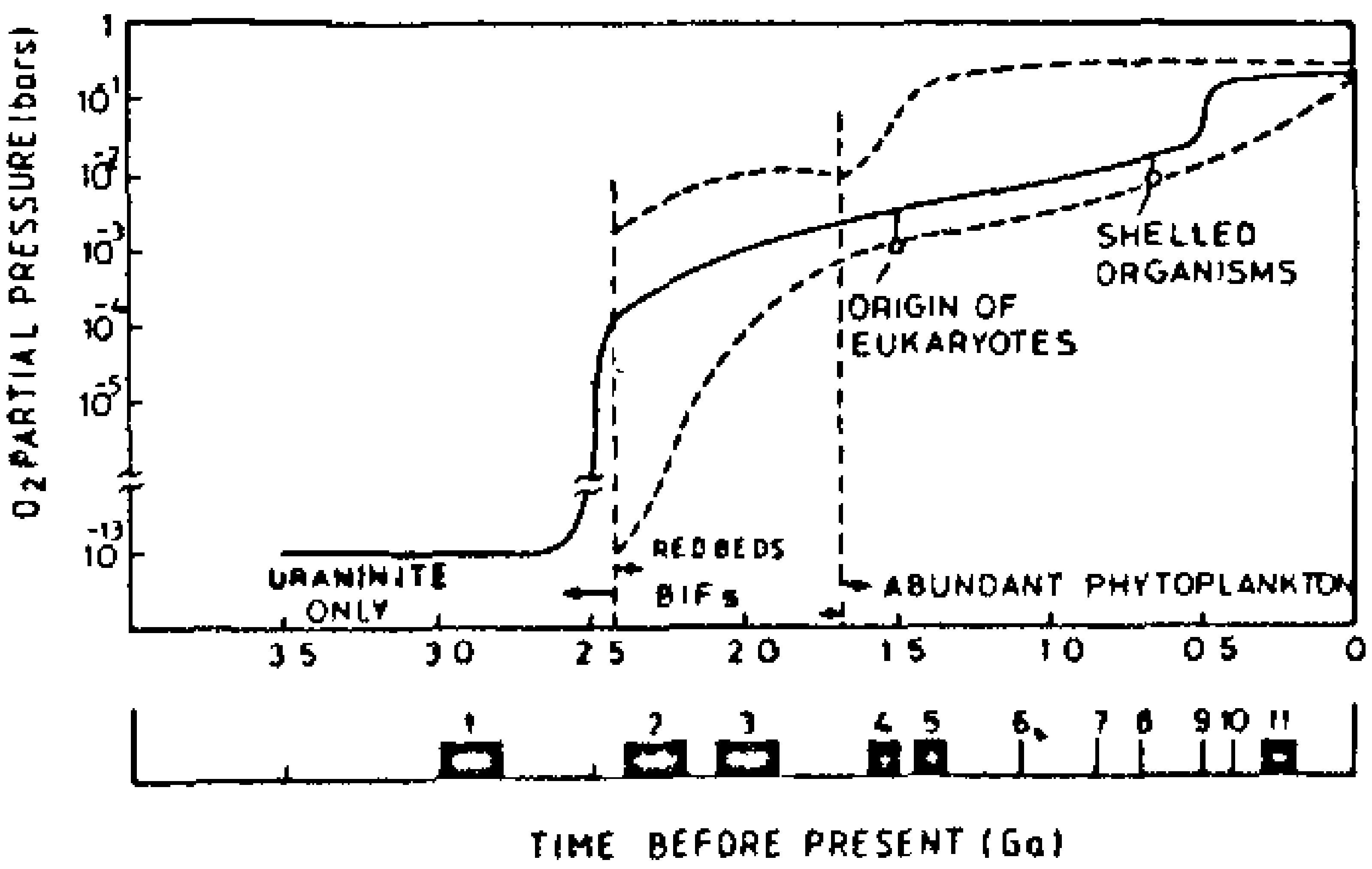

Figure 8. Relationship between the atmospheric O_2 level[11] and oxidation state of exogenous U-ores formed at different points of time. The solid curve is a 'best guess' while the dotted lines enclose range of uncertainty. Numbered black boxes bars at the bottom are position of successively younger exogenous U-deposits: 1, Dominion Reef, S. Africa (U^{4+} + pyrite); 2, Minas Gerais, Brazil [U^{4+}($\pm U^{6+}$) + pyrite], 3, Tarkwa, Ghana [U^{6+}($\pm U^{4+}$) + haematite], 4 to 8, and 11, unconformity-related (U^{6+}); 9 and 10, stratiform shale-hosted deposits (U^{6+})

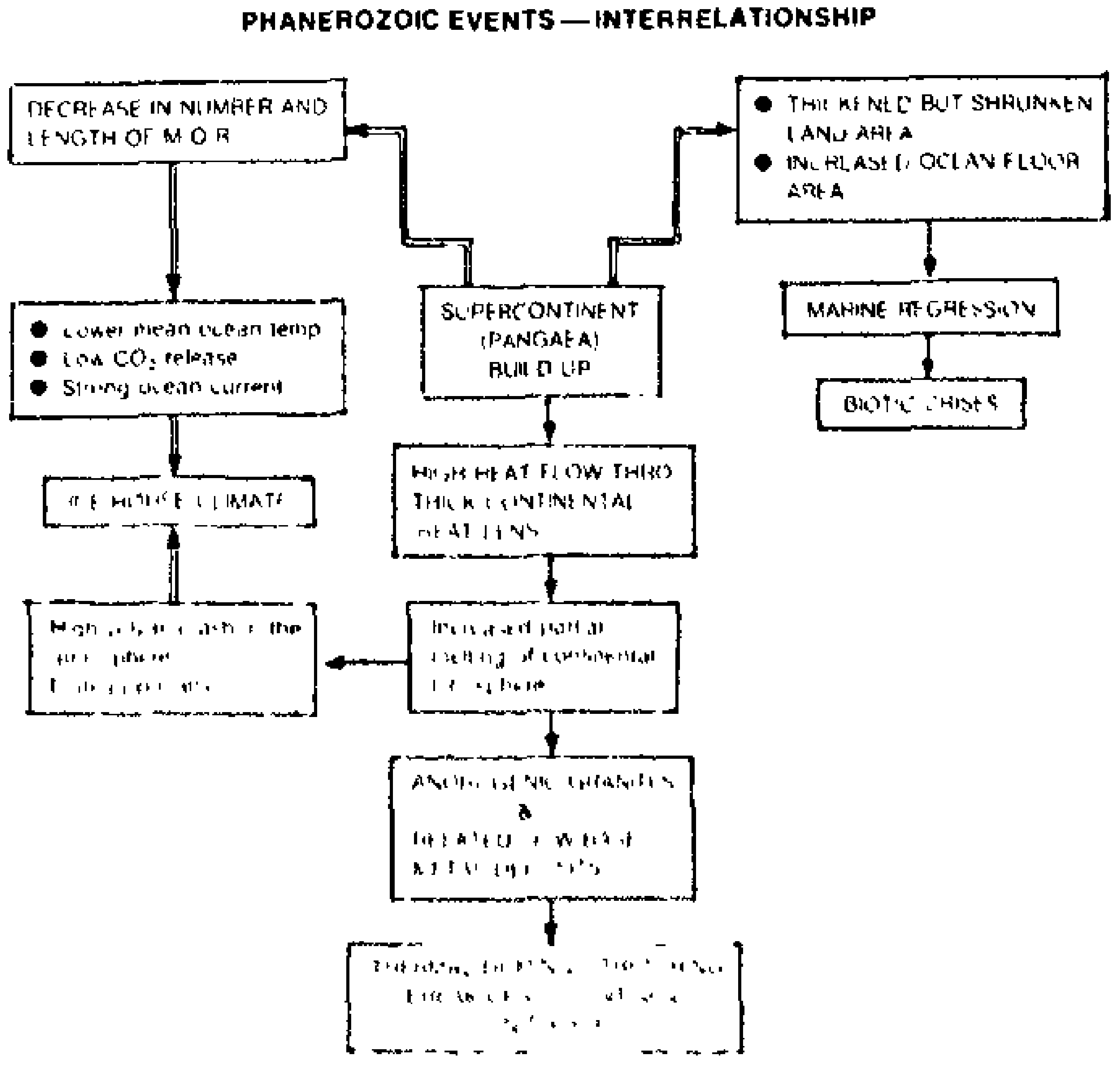

Figure 9. Interrelated geologic events/processes, including ore formation, caused by supercontinent build up

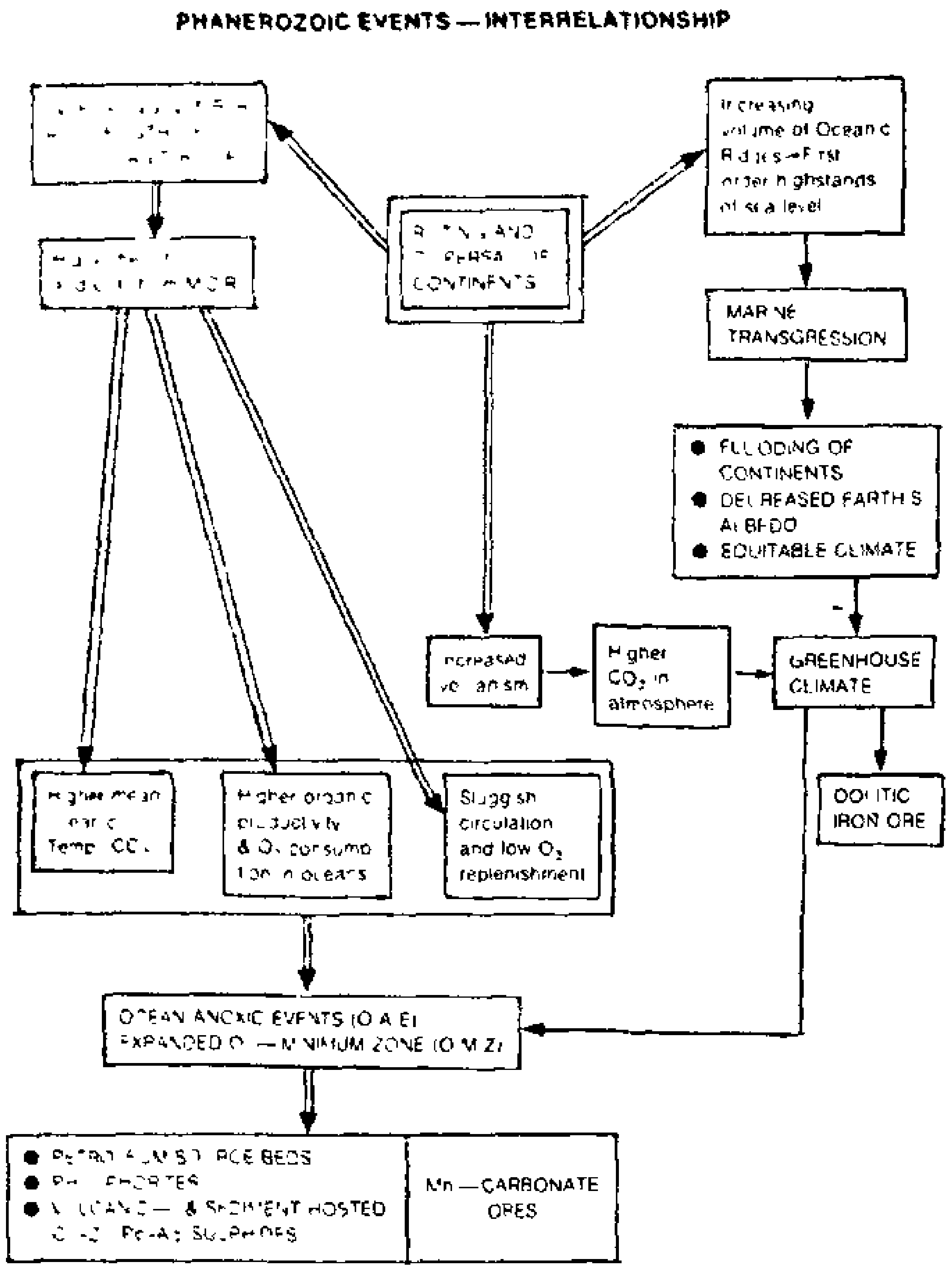

Figure 10. Interrelated geologic events/process, including ore formation, triggered by continental break-up.

planet. But, with available information, the rationale behind such preferential behaviour can only be outlined along its broadest contours. The space–time–process continuum that the earth's history represents can be perceived as an *n*-dimensional space where every single ore deposit obtains *n* specific coordinates. Only when all these coordinates are identified and rigorously determined for all known deposits can we expect to rationalize, fully, why ore deposits form *when* and *where* they do. The search for all conceivable coordinates is on, and it seems we have a long way to go.

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Design of crystal structure-specific surfactants based on molecular recognition at mineral surfaces

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The development of highly selective mineral processing reagents is urgently required in order to exploit the relatively difficult to process ore-deposits. Despite extensive research effort, there does not yet exist a comprehensive theory of reagent design. A critical review of past work suggests that new reagents should be not merely metal-ion-specific but also structure-specific. Both the choice of the functional group as well as the molecular architecture of the reagent is crucial to achieve the desired structure specificity. A systematic study of the separation systems where such structure specificity has already been observed and reported, would help delineate the appropriate interaction mechanisms required to accomplish it. A few examples are presented in this article to illustrate the concepts of structure specificity and molecular recognition, which are also of tremendous importance and of current research interest in the study of 'biomineralized' materials like oyster shells, corals, ivory and pearls.

Certain chemicals exhibit the characteristic property of enhanced adsorption at interfaces and hence possess the important attribute of being able to modify interfacial