

# A chemical approach to geological problems

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*One of the fundamental problems in geology, viz. crustal genesis and ore genesis, concerns how the continental crust on which we live and its associated mineral deposits, on which we depend more strongly today than ever before, were formed. A chemical approach allows a better understanding of this problem.*

Geology has been witnessing rapid progress in the past two decades because of the application of various branches of chemistry to understand earth processes and materials. Processes operate on materials and the present materials that we have on or near the surface of the earth are a result of past processes. Two major sources of energy drive these processes, the internal heat of the earth for the subsurface processes and the solar energy for the near-surface processes (Figure 1). Internal processes of the earth bring materials to the surface or near-surface areas dominantly by partial melting at deep interior where the ambient temperature locally and periodically exceeds the melting temperature of the materials present. During this process some chemical fractionation of the earth occurs because melting is partial and materials with lower melting temperature will preferentially enter the melt. Once materials are brought to the surface they are acted upon by the surface processes such as weathering, erosion, transportation and deposition. These processes modify and further fractionate the materials chemically during redistribution. Both types, particularly surface ones, of processes operate through the medium of water. Without water, cycling and recycling of materials would be inhibited and our planet also would be a dead one. Both the sources of energy are also being used up in the constant cycling of earth's materials, which again buffers the surface temperatures within a small range for life processes to start and evolve.

The resultant chemical fractionation of the earth has been a continuous process since the birth of the earth 4.6 Ga. This has been responsible for the formation of the earth's lithosphere, hydrosphere, atmosphere and finally the biosphere each with a distinct chemistry of its own.

In the evolving earth nothing is permanent except change. We talk about residence time even for chemical elements in various parts of the earth. For example; an

atom of Ce stays in seawater for about 60 years before it gets removed from it. On the other hand Sr can stay in seawater for several hundred thousand years before it gets removed. Similarly the latitude and longitude of a given place on earth change with geological time. The city of Bangalore which has the latitude of about 13°N and a longitude of 77.6°E was near the south pole before 200 Ma. Also, the entire New England area in the NE United States was thought to have been added to the North American continent 300 Ma. Prior to that it was part of the African continent. Thus even continents do not remain in one place and they could be assembled and separated.

Our interest is to unravel the mysteries of the dynamic earth in the formation of continents with their associated mineral deposits using an interdisciplinary subject called Geochemistry. It deals with the distribution of elements in different parts of the earth, migration of elements from one part to the other and the physicochemical laws governing their distribution and migration.

Elements in nature commonly do not occur in the elemental form excepting a few noble metals. This is because of free energy consideration which requires that

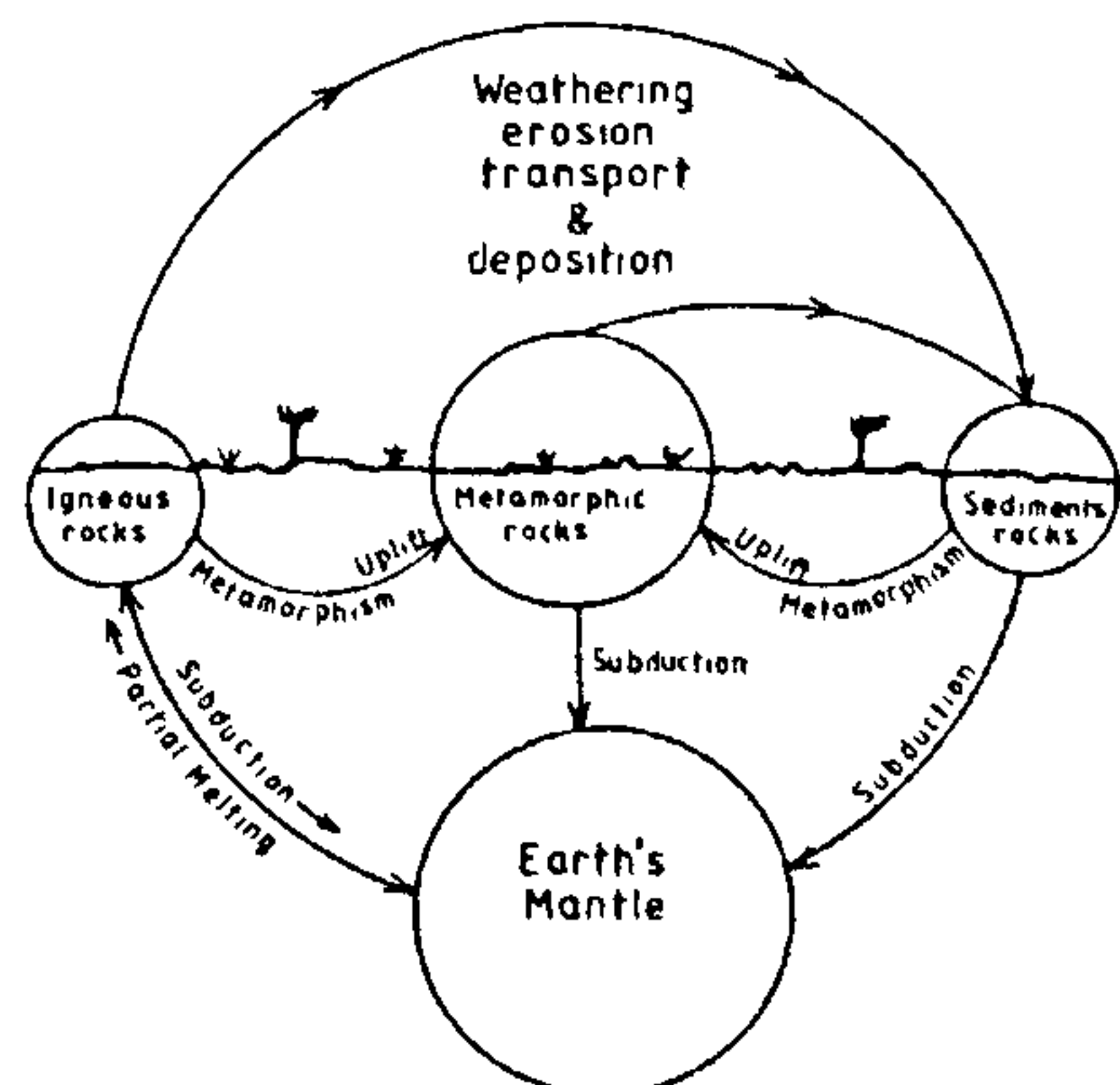


Figure 1. A schematic diagram of 'rock cycling'.

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elements combined would be far more stable (lower free energy) than individual elements existing separately. Therefore elements always combine to form compounds which geologists call minerals. What combinations are possible will be determined by atomic properties of elements present in and the prevailing physical conditions of any given system. Once minerals form, they are assembled in the proportion in which they were formed or in different proportions to form rocks and mineral deposits. Mineral deposits are simply concentrations of a particular or at best a few minerals in a proportion significantly higher than the surrounding rocks.

Rocks thus formed at different places and possibly at different times can be assembled together by large-scale subsurface processes (tectonic processes). The term crust is used for the aggregate of rock masses. These tectonic processes are again driven largely by the internal heat of the earth. The assembled rocks can also be disaggregated by subsequent tectonic processes. These crustal scale processes result in the formation of new mineral deposits as well as destruction of pre-existing deposits.

Thus the earth's crust is made up of rocks. Rocks are made up of minerals. And minerals are made up of elements. Geochemistry deals with the distribution and redistribution of various elements associated with all these micro- to megascale earth processes. By a careful study of elemental concentration in various rocks and their constituent minerals from a given piece of the crust we can place certain constraints on the formation and evolution of that part of the earth's crust. Through geochemical studies we can eliminate some processes and can suggest some possible ways of crust formation, i.e. we cannot be very definitive about the process. Even today geology is not a very precise science. Geochemistry, by quantitatively treating the chemical data, tries to make the earth system processes less and less imprecise.

Distribution and migration of elements are to a large extent controlled by their crystal chemical properties in minerals. Minerals have definite internal structures. Because atoms sit in symmetry-controlled crystallographic sites, minerals have commonly fixed stoichiometry. Certain atomic sites in mineral structures allow replacement of atoms of one element by those of others, which have similar valencies, ionic radii and electronegativities. Atomic sites in some minerals have a rigid geometry which allows only atoms of a particular kind and does not permit free substitution; for example, K in micas. We call that element for that mineral as an essential structural constituent (ESC).

There are certain elements which are present in the earth only at levels of a few micrograms or nanograms per gram of an average rock. These trace elements substitute for major mineral-forming elements in atomic

sites. Their substitution is commonly unlimited because they are present only in low concentrations. In many minerals cation sites allow replacement of one type of atoms by others; here the concentration of an element in a mineral is fixed by the stoichiometry and not by its abundance in the system. Such elements are called intermediate elements. This is because in terms of their solution behaviour these elements are intermediate between ESC and trace elements.

One of the thermodynamic properties of trace elements in mineral solutions is particularly useful in quantitatively evaluating rock-forming processes. During mineral (M) formation from, say, a liquid (L) at a constant temperature and pressure the mineral is in equilibrium, at least instantaneously, with the liquid. Therefore, for a given element:  $G_i^M = G_i^L$  at equilibrium, where  $G_i$  is the Gibbs free energy which is related to the standard state free energy,  $G_i^0$ ,

$$G_i = G_i^0 + RT \ln a_i \quad (1)$$

Therefore

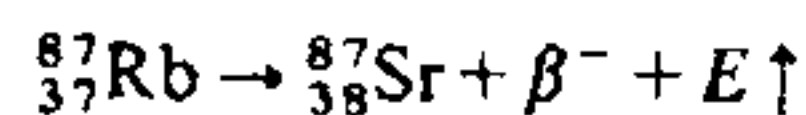
$$(G_i^{0,L} - G_i^{0,M}) / (RT) = \ln a_i^M / a_i^L = \ln K, \quad (2)$$

where  $K$  is the equilibrium constant, and

$$a_i = \gamma_i \cdot X_i \quad (3)$$

For ideal solutions  $\gamma_i = 1$  and for real solutions  $\gamma_i \neq 1$ . For major elements,  $\gamma$  depends on temperature, pressure, bulk composition of the system and on the concentration of the element itself in the system. For trace elements, however,  $\gamma$  does not depend on the concentration of the element in question. For a system at a given  $T, P$  and bulk composition,  $\gamma$  for a trace element is constant. Therefore, the equilibrium constant  $K = k(X_j/X_i)$ , where the ratio of the concentration of an element between the two phases is known as the distribution coefficient,  $Kd$ . Because  $k$  does not depend on the concentration of any given trace element  $Kd$  is a function of only  $T, P$  and the bulk composition of the system. In the earth the three variables are usually interdependent. The value of  $Kd$  is a measure of chemical fractionation during mineral formation. For major elements  $K = (\gamma_i^M / \gamma_i^L) (X_j / X_i)$ . Because the ratio of the activity coefficients may vary with concentration, for a given  $K$ ,  $Kd$  may have to vary with the concentration for a major element.

Certain trace elements in the earth such as, for example, Rb, Sm, U and Th have unstable nuclei which by the emission of alpha and beta particles decay into stable isotopes of other elements. For example,



$$({}^{87}_{37}\text{Rb})_t = ({}^{87}_{37}\text{Rb})_{t_0} \exp(-\lambda t) \dots \dots \text{decay of parent,}$$

$$({}^{87}_{38}\text{Sr})_t = ({}^{87}_{37}\text{Rb})_t [\exp(\lambda t) - 1] \dots \dots \text{growth of daughter,}$$



where  $\lambda$  and  $t$  refer to decay constant and time, respectively. Thus the growth of  $^{87}\text{Sr}$  from  $^{87}\text{Rb}$  is a time-dependent process. We use the concentrations of radioactive parent nuclide and radiogenic daughter nuclide to estimate the time of formation of rocks, the source characteristics and the subsequent geological history of rocks.

Trace elements are therefore important in understanding earth processes. In addition many important ore metals such as, for example, Cu, Ni, Cr, U, Th, which we use in our industrialized civilization occur as trace elements in the earth.

Our approach to geological problems involves (i) the study of rocks in the field for their mutual temporal and spatial relations and for their stress-strain histories, (ii) determination of their mineral assemblages, (iii) determination of the concentrations of various major and trace elements and isotopes of certain trace elements and (iv) modelling of the elemental, including isotopic, concentrations using simple concepts from thermodynamics and petrogenesis. The ultimate purpose of all these exercises is to chase down the earth processes responsible for the formation of that piece of the crust and its associated mineral deposits.

Let me illustrate the approach by considering the area around the famous Kolar Schist Belt. The Kolar belt is well known for its economic gold mineralization. It is one of many belts in the Dharwar Craton. All the belts consist of metamorphosed volcanic and sedimentary rocks. These belts are surrounded by a sea of plutonic granitic rocks. These rocks are thought to have been formed during the time interval between 3400 and 2500 Ma. It is however not known how and where these rocks were formed and how they were assembled to make up the stable continental crust known as the Dharwar Craton. We also do not know how the gold deposits present in some of these belts were formed. An intensive study of a small area will potentially enable us to evaluate the major processes responsible for the formation of the Dharwar crust.

The Kolar belt is a 80-km-long and 3–4-km-wide belt (Figure 2). It dominantly consists of a group of basaltic rocks and minor amounts of felsic rocks and banded iron formation. The rock association and some structures preserved in them indicate that the rocks were formed under subaqueous environment. Their present structures and mineral assemblages suggest that the rocks were taken down, after their initial formation, to a depth of about 6 to 10 km and were subsequently uplifted. In this process the rocks were deformed and metamorphosed. Gold mineralization is found in all rock types. There are two types of deposits, one associated with quartz veins and the other with sulphide minerals.

The belt is surrounded on all sides by granitic rocks. The contact between the belt and the surrounding rocks

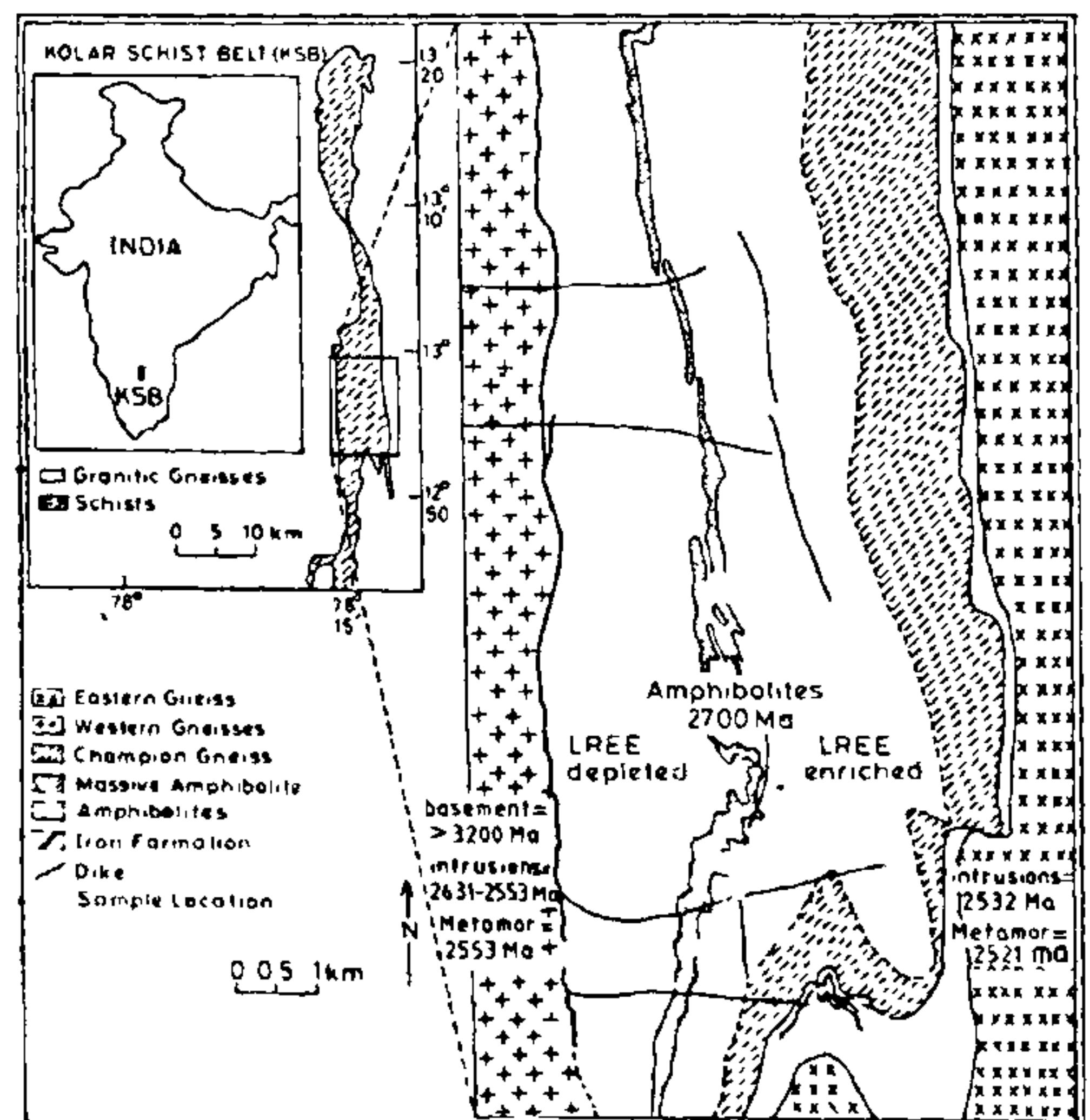


Figure 2. A generalized geological map of the Kolar Gold Fields area. Also shown are the ages of various rocks.

on all sides is sharp, i.e. tectonic. This implies that the two groups of rocks could not have formed together in their present place. Rocks of both the groups are flattened in the N–S direction, multiply folded with fold axes trending roughly in the same direction and granulated in the contact zones. These deformational features are suggestive of strong horizontal E–W compression to which all the rocks were subjected.

The major element chemistry of the rocks of the belt is useful to evaluate the physical conditions of melt generation for these originally igneous rocks. From the major element composition we calculate the concentration of Mg and Fe in the melt which was in equilibrium with the dominant mineral of their solid source. In Figure 3 we have shown the compositions of melt fields in the Mg–Fe space for partial melting of a solid source at three different pressure conditions. For the earth, generally pressure and temperature are dependent variables. In the Mg–Fe diagram the Kolar basaltic rocks plot as two different groups with a distinct gap between them. One group of rocks has distinctly higher Mg concentrations. Their melts must have formed at pressures greater than 30 kilobars and temperatures greater than 1450 C (corresponding to depths greater than 100 km). These rocks are called komatiitic basalts. The other group of rocks with lower Mg concentrations, called tholeiitic basalts, were formed at pressures less than 15 kbar, i.e. shallower than 50 km depths. These physical conditions of melt generation are commonly available in the earth's mantle. Melts derived from

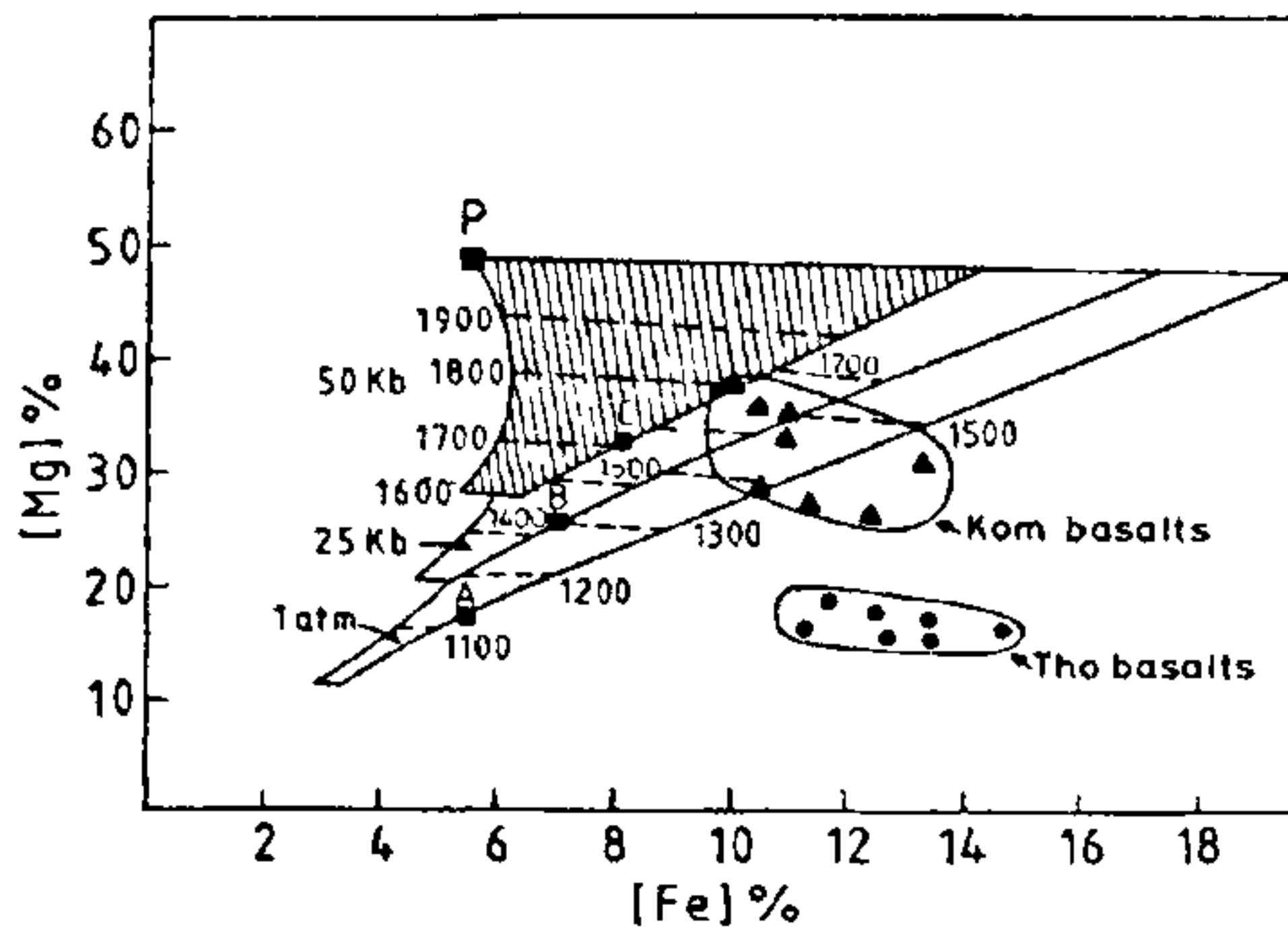


Figure 3. A plot of Mg versus Fe concentrations in the Kolar basaltic rocks. The melt fields for various pressures give the composition of melts generated from a source P if partial melting occurred over the indicated temperature range for each pressure. Note the Fe enrichment in all rocks, which is a result of the sources having higher Fe/Mg ratios than the reference source P. A, B, C refer to solids at 1 atm, 25 and 50 kb pressures, respectively.

distinct regions of the mantle were found in 3-4 km wide belt. This occurrence is rather rare and points to rift-related volcanism provided the two groups were contemporaneous in a geological sense.

Let us now see what the trace element data of these rocks tell us. We will use the abundances of lanthanide series of rare earth elements (REE) in these rocks. REE occur only to the extent of a few to few tens of ppm in these rocks. Commonly the abundances of REE are normalized to a chondritic mantle (REE pattern) so that inter-elemental variations are smoothed and the relative enrichment of a rock with respect to the mantle can be used to infer processes of rock formation and their source characteristics. Representative REE patterns of the two groups of basaltic rocks are shown in Figure 4. The rocks have much higher abundances of REE relative to a chondritic mantle.  $K_d$ 's for all the REE between major mantle minerals and melts are much less than even 0.1. Therefore REE are enriched in the melt during partial melting irrespective of physical conditions. The magnitude of enrichment usually is an inverse function of the extent of melting.

The REE chemistry of basalts in Figure 4 is quite variable in terms of both abundances and patterns. Although the variations in abundances can be explained by differences in the percentage of melting, detailed calculations suggest that the mantle had variable REE abundances. Most sources had a previous history of depletion and were then variably enriched in REE. Within the small Kolar belt we have basaltic rocks whose sources are as variable as those of the present-day oceanic areas, i.e. ridges, islands, floor and island arcs.

In order to estimate the time of formation of these

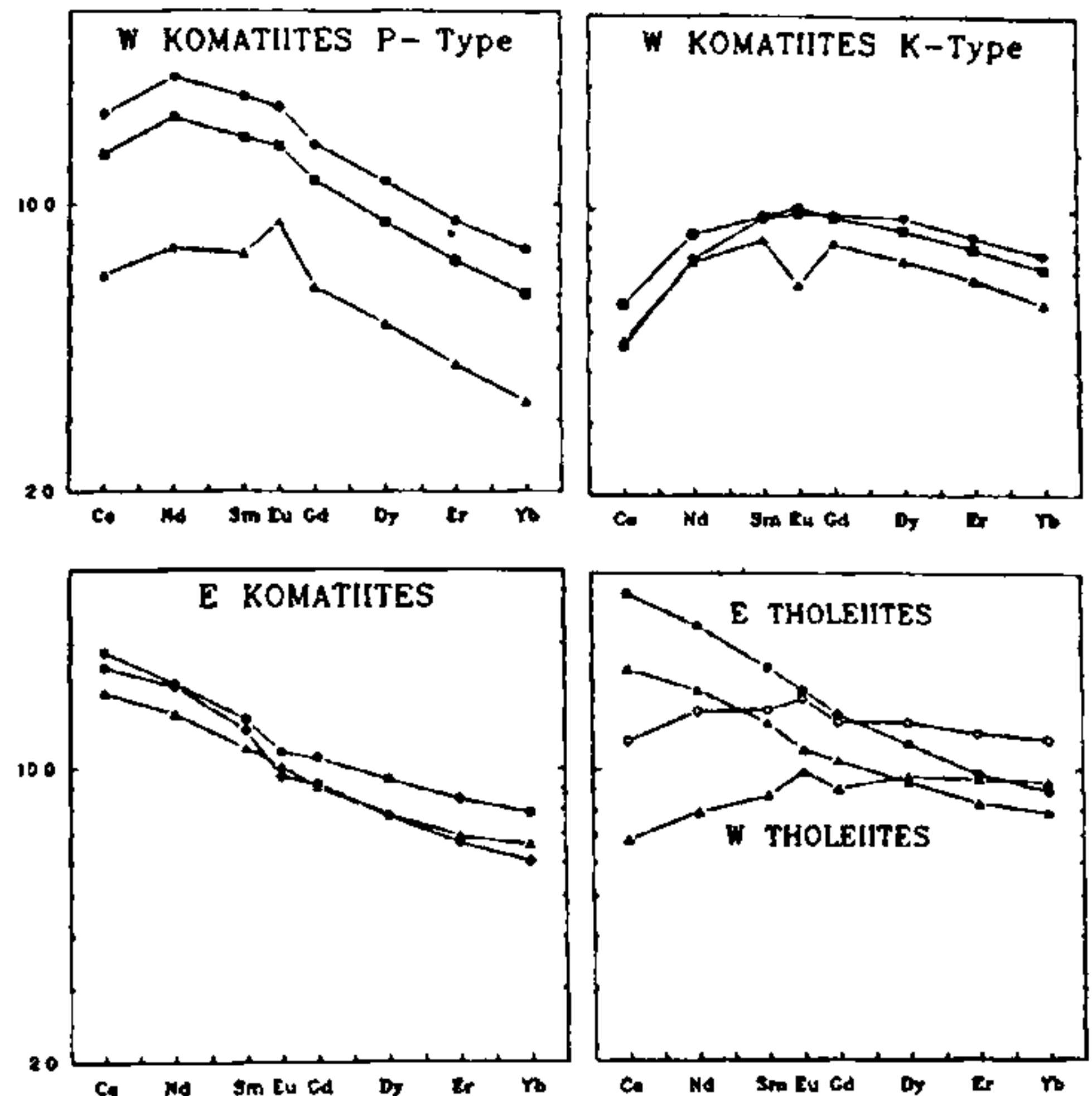


Figure 4. Chondrite-normalized REE abundances in Kolar basaltic rocks. Note that the east side rocks show enrichment of low-Z REE (LREE). Rocks on the west side show varying amounts of LREE depletion.

basalts we have used two isotopic systems. The Sm-Nd system on komatiitic rocks gives an age of about  $2696 \pm 136$  Ma (Figure 5). The Pb-Pb system based on the decay of the two U isotopes on a group of tholeiitic basalts gives an age of about  $2732 \pm 155$  Myr (Figure 6).

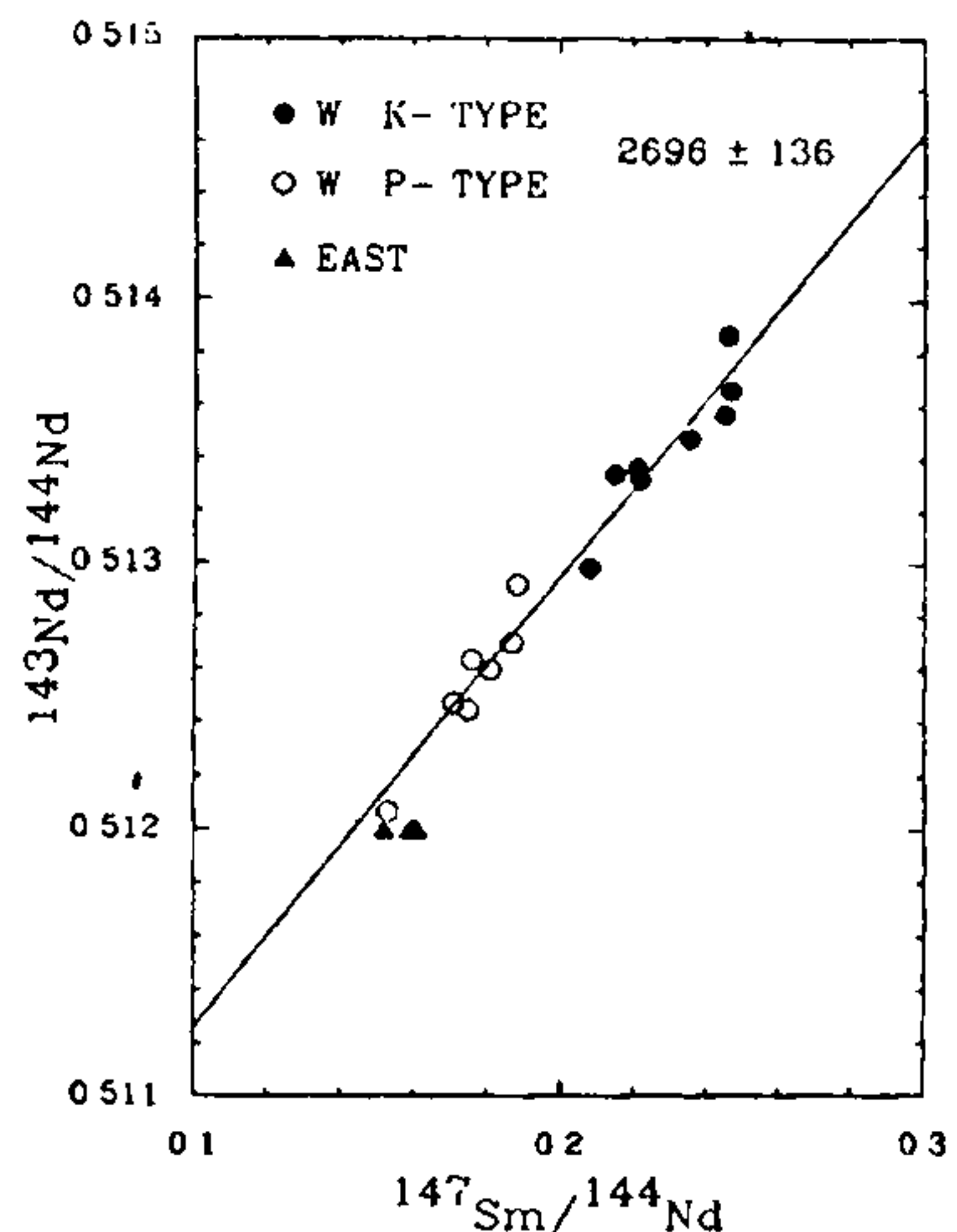


Figure 5. Sm-Nd isochron plot of Kolar komatiitic basalts. K and P refer to different degrees of LREE depletion in the west side rocks.



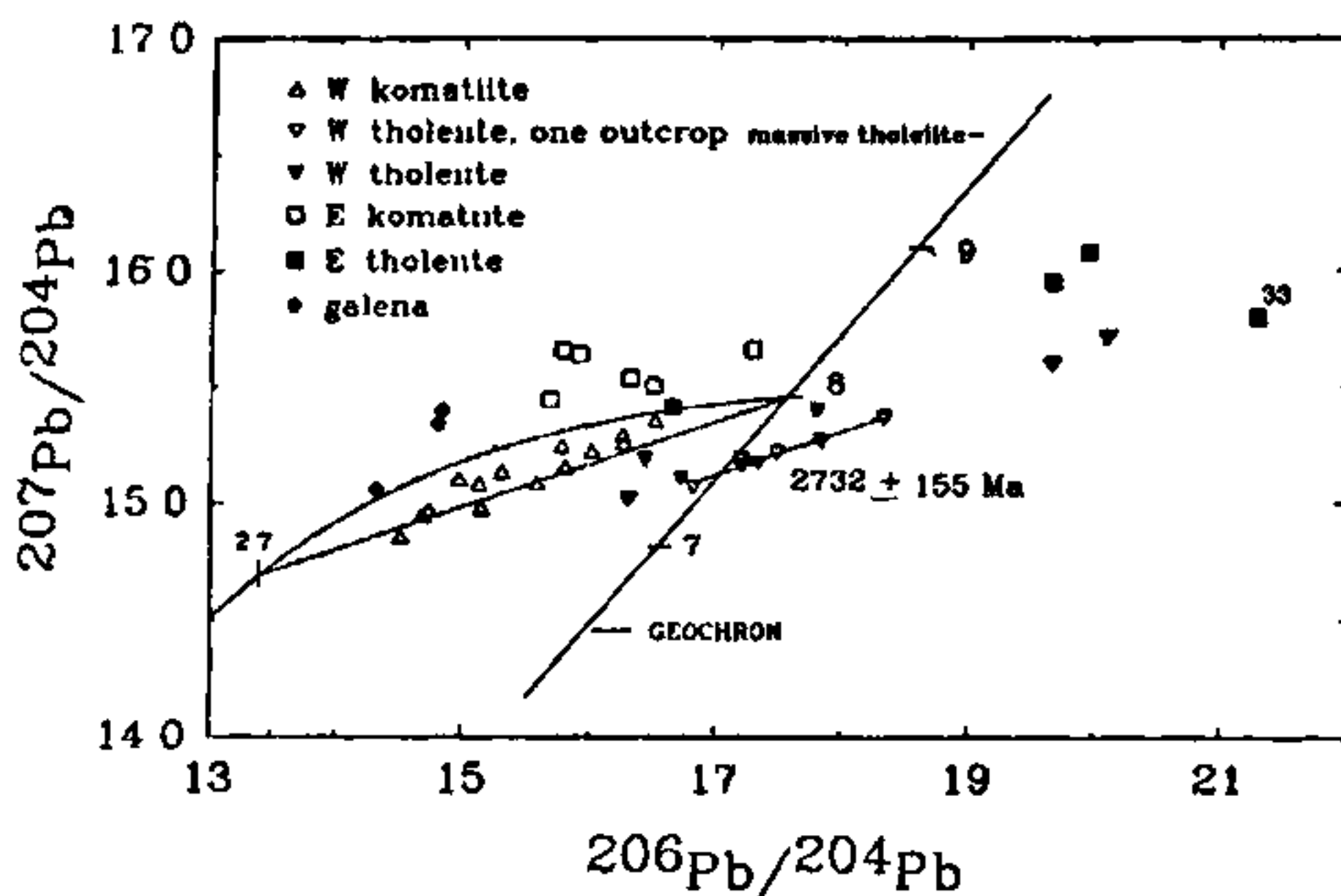


Figure 6. Pb isotopes in Kolar basaltic rocks. Note that the west tholeiites give an age of  $2732 \pm 155$  Myr.

Thus the two groups of rocks are of very similar age. In oceans today basaltic rocks range in age between 0 and 180 Myr. Therefore the contemporaneity of the two groups of basalts permits the possibility of these rocks having been emplaced in different parts of an Archaean ocean.

The granitic rocks present on either side of the belt have many differences in their major and trace elements, including isotopic characteristics. On the west side the granitic rocks have a large range in major and trace element composition. Although a majority of rocks were formed from mantle sources there exists a rock type which had formed from a pre-existing granitic crust (Figure 1). Mantle-derived magmatic intrusions occurred on this side between 2630 and 2550 Ma. The period of peak metamorphism occurred about 2550 Ma. Mantle-derived magmas were isotopically contaminated by at least 3200-Myr-old granitic crust. The geological history of this side has a strong semblance to active continental margins of the present-day plate regime.

In contrast, on the east side of the belt granitic rocks are more uniform in composition as well as in the age of formation. These rocks were formed around 2532 Ma either directly from the mantle or from a very shortlived basaltic crust. Shortly after formation the rocks were metamorphosed around 2520 Ma. There is no evidence in major isotopic systems, such as Rb-Sr, Sm-Nd, U-Pb, for any older crustal contamination.

What is intriguing is to note that when the east side granitic rocks were affected by a strong thermal event 2520 Ma, the west side rocks which are only 4 km away were not affected by the same thermal event. This is unlikely if the two granitic terrains were separated by only 4 km. A possible implication of all these differences is that the granitic terrains on either side of the Kolar belt were geologically distinct until about 2520 Myr ago. These two granitic terrains were possibly separated by

an ocean, the rocks of which are represented by those occurring within the belt. All the rocks of this area bear a common cooling age of about 2420 Myr. We interpret this age information to suggest that the two continental terrains and the oceanic terrains were brought together in the time interval between 2520 and 2420 Ma by large-scale earth processes similar to modern plate tectonics.

What is the significance of this study? We know that plate tectonics operate today, moving continents around and adding new crustal materials to them. In the records of earth history there are geological evidences for the existence of plate tectonics as far back as 600 Ma. But as we go back further in time geological evidences for plate tectonics are obliterated and therefore the nature of tectonic processes responsible for the crustal growth is a subject of great geological controversy. With the integrated chemical approach we could extend the plate tectonic model for crustal growth as far back as 2500 Ma.

Finally let us look at the gold deposits present in the belt. The sulphide gold deposits are associated with iron formation. Their chemistry, particularly REE (Figure 7), resembles that of the hydrothermal sulphidic sediments that are being deposited today on the ocean floor near mid-ocean ridges. It is possible then that gold mineralization started right from the time of basic magma emplacement on the ocean floor. Economically more important gold is associated with quartz veins. Chemical, including isotopic features of the metamorphosed host basalts, altered wall rock to the veins and the ore veins themselves indicate that the solutions responsible for the ore veins were derived from the metabasalts during the several episodes of deformation and metamorphism associated with the protracted period of compression and eventual juxtaposition of the continents. Metamorphosed basalts even at amphibolite grade deformed in a brittle manner to cause focused flow of ore solutions to cause ore vein formation. Thus

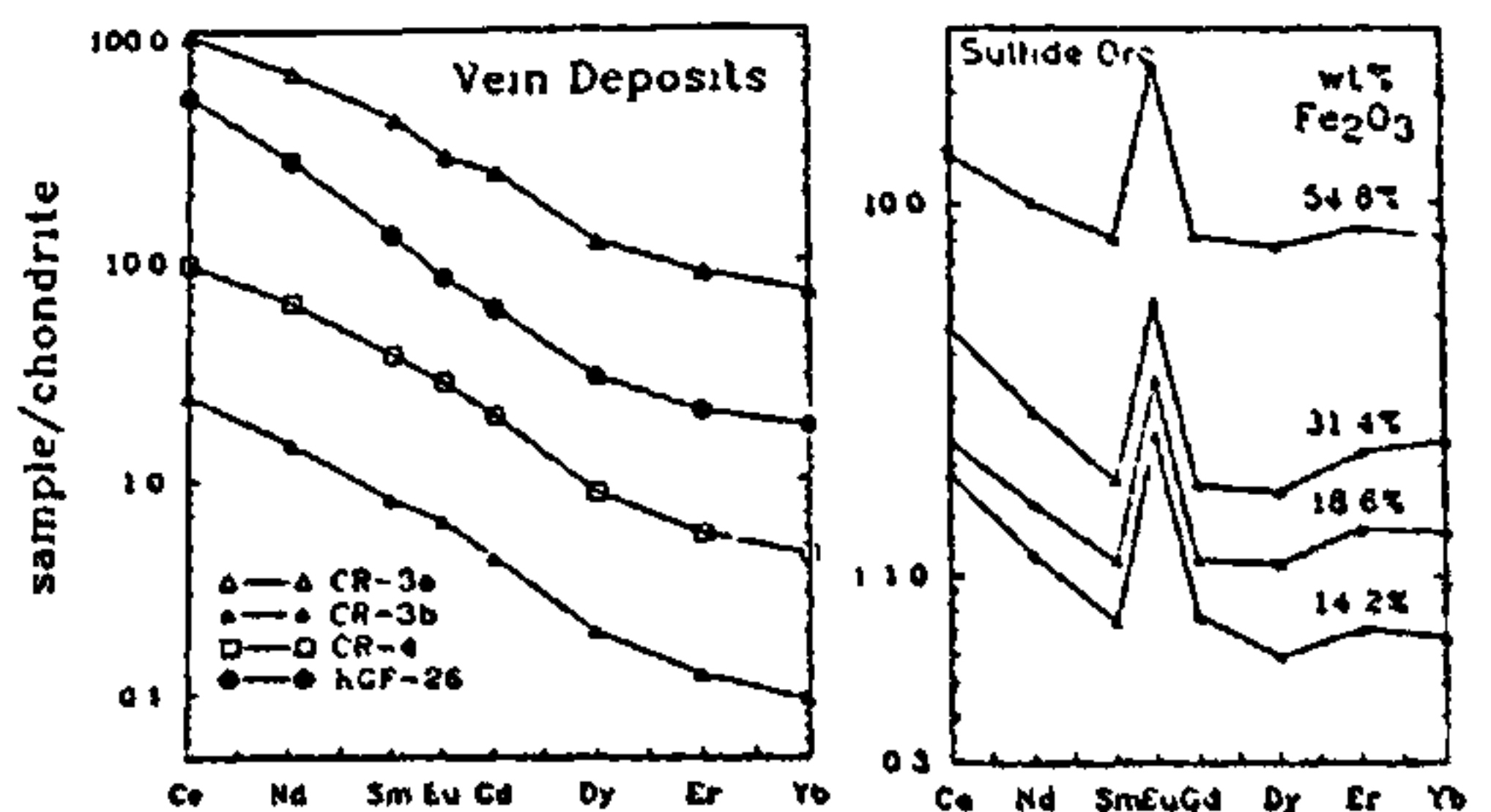


Figure 7. Chondrite-normalized REE abundances in the two different gold ores in the Kolar belt. The REE patterns of the sulphide ore are similar to those of the hydrothermal sediments deposited near the present-day ocean ridges.

the most important gold mineralization is likely to be a result of the same tectonic processes that caused crustal accretion.

### Conclusion

Geochemistry is a powerful tool in earth system science. We need to have the technical capability to generate high quality geochemical data. Such skill is

generally lacking in India today. The development of this skill is essential for modern research in earth science.

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# The compromise between seeing spatial layout and making visual discriminations

G. Adrian Horridge

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*Insect vision, which is simple compared to human vision, provides many clues for the design of artificial visual-processing mechanisms. Such artificial mechanisms based on insect vision are likely to have applications in artificial-intelligence systems.*

Our fascination with the marvel of human vision and our lack of information about the real mechanisms are two major obstacles to be overcome before the mechanisms of simple low-level visual discriminations can be copied into technology. The first obstacle is avoided by considering the vision available in lower animals and the second by analysis of behaviour, electrophysiology and microcircuitry of their natural visual mechanisms where we can. The appropriate level of complexity, minimal for making a visual system for manoeuvring in the three-dimensional world, is that of a generalized insect, which conveniently indicates one practical compromise between complexity, performance and ease of understanding. Unlike human vision, which relies extensively on a huge memory and rapid learning, insect visual mechanisms are relatively simple in that they certainly see the outside world very well but there is little analysis of two-dimensional pattern, and objects are not categorized into classes.

A camera, or a video camera attached to a television screen, can only transfer the image from one place to another. Vision is quite different in that it involves discrimination of certain features of the image followed by decision and action. A visual system must therefore

be designed with reference to what features of the outside world are adequate cues, and what actions will follow. The design must be directed at abstracting some cues from the image, and for economy it need do no more. A good example is the automatically opening door (Figure 1,c) which detects the arrival of a shadow and opens the door for a short time. For low-level vision, there is no need to copy human vision or reconstruct the spatial relationships of every detail in the outside world.

We have little vision technology at this intermediate level. Examples are surveillance equipment that set off an alarm if an intruder enters the field of view in an otherwise stationary scene, the guidance of a heat-seeking missile by infrared radiation, the automatic landing equipment on aircraft that use radar waves, and the range-finder on some automatic cameras that use sonar (Figure 1). All these simple kinds of eyes share the common features of eyes, namely sampling in angular space and use of some part of the total visual information.

The eye operates by having many receptors that look in different directions at the same time (Figure 2), so that information is transmitted into the eye in many channels in parallel. The video camera works quite differently, in that it scans the image one pixel at a time and transfers the raster pattern into a long time series, which can regenerate the picture on a TV screen by replay of the raster to bring together the picture. We

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