Diagenetic rare earth phosphates – Promising minerals for Precambrian sedimentary geochronology

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To geologists, the concept of time is fundamental in tracing earth's evolution, and they measure this in units of millions of years, the span geological processes take to operate. The few hundred million years (m.y.) following earth's accretionary phase, 4.56 billion years (b.y.) ago, were turbulent and it took some time for the crust that kept forming from molten early earth to remain stable and grow to large land masses, get eroded and form sedimentary rocks. Myriad other terrestrial events also occurred in this period which, like the milestones on a highway, served to mark boundaries dividing the Precambrian to the Present, an enormous time-span, into eras, periods and systems.

The Precambrian (4500–570 m.y.) and Phanerozoic (period < 570 m.y.) form two broad divisions of geological time. The Phanerozoic is further divided into Palaeozoic, Mesozoic and Cenozoic eras and based on the appearance or disappearance of specific animal life seen as fossils in rocks, these eras are subdivided into relatively narrow intervals, less than 100 m.y. apart (biostratigraphic division; Figure 1). But in the earlier time-span of Precambrian, which is divided into Archaean and Proterozoic periods, the fossil record is very poor and biostratigraphic methods are not helpful to reduce further the duration these two periods occupy. Therefore, terrestrial events other than faunal records, like occurrences of igneous intrusions, episodes of volcanism, metamorphism or mountain building were much relied upon to build relative chronologies, though inferences from such events were often inconclusive or uncertain. Nonetheless, they formed a reasonable basis for establishing divisions in the Precambrian strata of many countries.

A survey of the Indian Precambrian areas in southern and eastern India, parts of Assam, Bihar, Madhya Pradesh, Rajasthan, Sub- and Central Himalayan regions shows vast time segments occupied by sedimentary rocks such as quartzites, sandstones, limestones and shales, interspersed by conglomerates or other beds. All these formations occupy a span of 1600 m.y. from early Proterozoic (2500 m.y.) to late Proterozoic (900 m.y.)[1,2]. These strata are presently correlated with major orogenic events at 2.6, 1.5 and 0.8 b.y. or granitic episodes at roughly 300–500 m.y. intervals between 3.6 and 0.1 b.y. or episodes of dyke volcanism at 2.7, 1.8, 1.5, 1.2 and 1.0 b.y. (ref. 1). But, they occurred intermittently and at long stretches of time, therefore, remained poorly correlated and divided.

The discovery of radioactivity in 1905 and recognition of its potential to date rocks was a great turning point in earth scientists' attempts to quantify the march of geological evolution. With the gradual development of radiometric dating techniques in the following decades, the complexion of Precambrian geology and chronology changed for the better, though the application of radioactive dating was confined mostly to igneous and metamorphic rocks or minerals in them. Also, the dates obtained had error-ranges plus–minus 100 to 200 m.y. a stretch of time which in younger Phanerozoic is well divided into 2 or 3 distinct periods. The reason for this state of

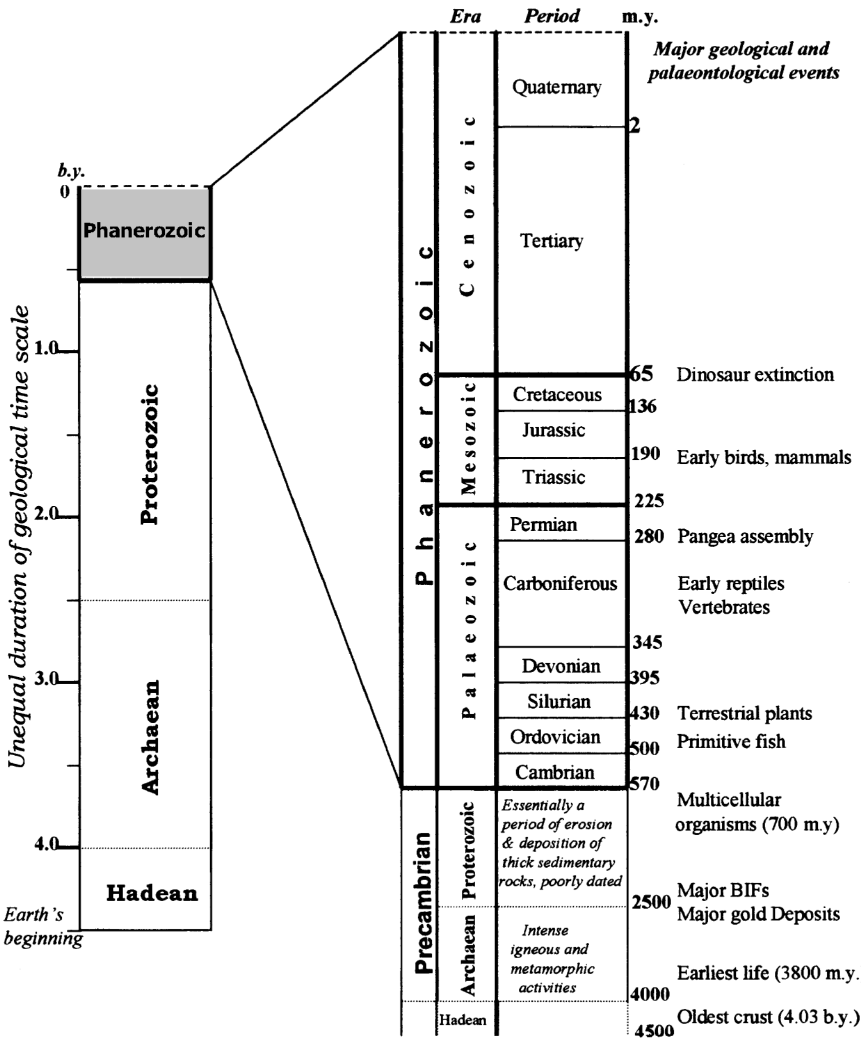

Figure 1. Geologic time scale showing some of the geological and palaeontological records used for time-division of the Precambrian and the Phanerozoic eons.

Precambrian chronology is lack of proper radiometric dating and correlation of sedimentary formations occupying sizeable geological time in many countries. Dating them using conventional minerals like zircons, which are normally detrital products in these rocks, would give only the ages of their igneous parent. Thus, the duration of major geological eras remained unequal – the Precambrian era stretched for 4 b.y., while the succeeding Phanerozoic was well divided into Palaeozoic, lasting 345 m.y., the Mesozoic, 160 and Cenozoic, 65 m.y. (Figure 1).

From time to time, attempts were made to introduce fresh subdivisions to the Precambrian based on several new studies and terrestrial records. For example, the date of the oldest preserved crust (4.03 b.y. ago) or earliest appearance of bacterial organisms (3.8 b.y. ago) or the major gold and iron deposits (around 2.8 b.y. ago), served as tentative boundaries between Hadean and Archaean and Proterozoic (Figure 1), but even these happen to be spaced several hundred m.y. apart[3,4]. Even though geologists are aware of this unequal division, the situation could not be improved in the absence of suitable minerals to date the sedimentary rocks occupying the unresolved Precambrian time. Such minerals should also have formed during or soon after the accumulation of deposits in the basin and must contain small amounts of U and Th. Further, the mineral should be impervious to entry of Pb during crystallization and must retain the radiogenic lead, without loss, to permit age calculations. Although many new minerals are generated in the sedimentary basin, not all of them meet these requirements and also occur in an easily retrievable manner for carrying out the mass spectrometric analysis.

In a sedimentary basin, the gradual increase of pressure and temperature from ever-growing thickness of detritus affects the stability of diverse minerals, which are brought from different source rocks to the basin. These minerals normally cannot co-exist (incompatible) under the conditions their parent rocks formed, but are now forced to remain in a state of non-equilibrium in the basin. However, through several physical and chemical changes, collectively called 'diagenesis', they strive to attain equilibrium. This diagenetic process results in compaction of sediments, alteration of the minerals or their dissolution or replacement, as well as cementation of the grains in the pile. Compaction results in squeezing out the pore-water, which becomes an agent for dissolution or alteration and a good medium of transport of the dissolved phases (Figure 2). Chemical evolution of this diagenetic fluid results in precipitation of new minerals – a process termed 'authigenic crystallization'. Classic examples of this process are the conversion of opaline silica-shells to quartz, aragonite to calcite, unstable smectite-clay to stable illites, precipitation of complex Fe, K, Mg silicates (e.g. glauconite), development of quartz and calcite as intergrannular cementing materials, formation of zeolites and even oil. Interestingly, a few phosphate minerals that carry rare earths, U and Th, like fluorapatite (Ca-phosphate), monazite (Ce-phosphate), xenotime (Y-phosphate) and crandalite (Al-phosphate) are also formed[5,6] and these minerals, according to a couple of current investigations[7,8], are promising for use in sedimentary geochronology and may help in refining Precambrian time scale.

Among the diagenetic minerals, glauconite, a hydrous silicate of Fe and K, has long been used for K–Ar, ^{40}Ar–^{39}Ar, and Rb–Sr dating of sedimentary rocks. Glauconites separated from conglomerates and sandstones from Precambrian Cuddapah and Vindhyan formations in central and southern India have given ages between 1276 and 722 m.y. (refs 9–12) and shales from the Mesozoic Bhuj formations in western India have yielded an age of 105 m.y. (ref. 13). Glauconite dates, however, are not much relied upon as doubts exist about the mineral's origin, whether authigenic or detrital, and its ability to remain unchanged in its K and radiogenic ^{40}Ar contents. Further, this method of dating is most effective only for formations younger than 200 m.y., with glauconites having $\geq 6.5\%$ K_2O (refs 13 and 14). Against the background of these shortcomings, the recent selection of diagenetic monazite[11] and xenotime[7] to date Precambrian sedimentaries, appears encouraging.

Diagenetic phosphates – fluorapatite, monazite, xenotime and crandalite carry minor amounts of U and Th and occur in formations like sandstones as minute pore-fillings or enmeshing other grains. Authigenic monazite, forming cores of marine nodules, has been used for U–Pb dating of certain sedimentary rocks[7]. In a recent study[8], xenotimes of undoubted authigenic origin from Precambrian sandstone in Australia have been similarly dated. These xenotimes mostly occur as overgrowths on detrital zircon (Figure 2), which has structural similarity (isostructural) and hence offers nucleation sites for precipitation of xenotime[8]. Its useful-

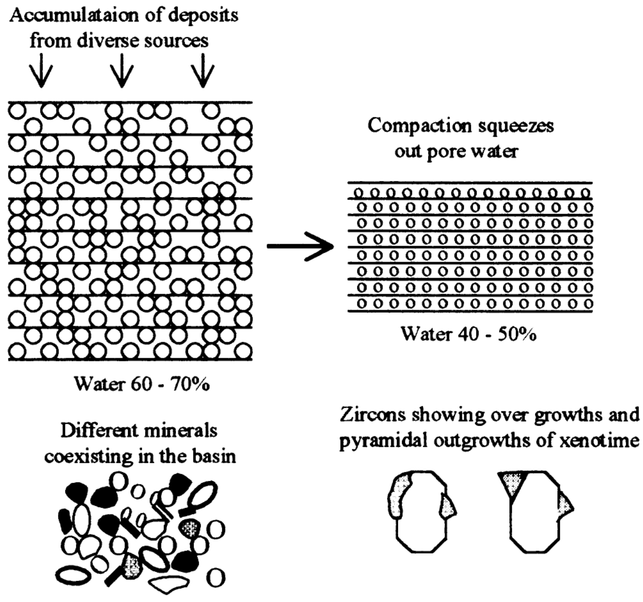

Figure 2. Diagenetic process in a sedimentary basin leading to compaction of sediments and release of pore water which carries dissolved chemical phases leading to precipitation of new minerals. Detrital zircons in the mixture of sediments offer nucleation sites for xenotime to precipitate.

ness for geochronology lies in the fact that it carries small amounts of uranium (~ 0.1%), inhibits entry of Pb and diffusion of original U and radiogenic Pb subsequent to crystallization. But, the mineral's tendency to occur as overgrowths on zircon grains and difficulties in its extraction as pure concentrate for mass spectrometry must have been reasons for ignoring it so far in sedimentary geochronology.

Now, the development during the 1970s of an *in situ* microanalytical dating technique[15], SHRIMP (sensitive high resolution ion microprobe), has been a boon to geochronologists faced with problems in handling very small amounts of sample and achieve high sensitivity. This instrument has high mass resolution and high transmission and the sample volume required, unlike in other isotopic dating methods, is orders of magnitude smaller. No physical separation of the xenotime to be dated is required. Instead, vapourization of micron-sized area of the mineral, directly from the polished rock specimen, using a beam of oxygen ions precisely focused on the site provides enough material for the mass analysis. In this way, diagenetic xenotime dates of two Proterozoic sandstone units in NW Australia, which were earlier age-bracketed in the range 1790 to 750 m.y., could now be accurately dated as 1704 ± 7 and 1704 ± 14 m.y. old.

Uraniferous rare earth phosphates are not unusual and are known to occur in several Proterozoic sedimentary formations, in some places in rich amounts[16]. The occurrence of zircon, a very common detrital mineral in many sedimentary horizons should prompt searches for the likely development of xenotime as overgrowths on it, the two being isostructural. Authigenic monazite, however, has not been extensively observed though the conditions for their formation are present in several sedimentary strata. The major hurdle, viz. the recovery of such diagenetic minerals present in small amounts, often as inseparable intergrowths or overgrowths can now be overcome with tools like SHRIMP or CAMECA1270 (developed at UCLA in 1980s) capable of targeting directly on micron-size sample site without the need to physically separate the mineral. Steady additions of dates, with increasing use of such probes will enable fixing absolute dates for several of the doubtfully correlated Precambrian sedimentary formations and usher in better resolution to existing broad time scales. With vast time-segments of Precambrian India occupied by sedimentary rocks, the availability of datable authigenic minerals like xenotime and monazite has also to be explored to achieve better global correlation and establish well-resolved boundaries based on absolute chronology.

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