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## Preface

## The first billion years: new insights from geochemistry $\stackrel{\leftrightarrow}{\sim}$

Prologue: (V)ast globes... after reaching the last stages of ebullition, were covered with scoriae like bubbling foam. And the crust which covered the molten matter of the globe and which hardened from the fused condition would be like scoria, as happens with metals in the furnace. If then the great framework of the earth, the exposed rocks, the imperishable silicates, are almost entirely vitrified, does that not prove that they arose from a fusion of bodies, brought about by the powerful action of nature's fire on still soft material? It is everywhere true that the most simple and primitive material in the composition of the earth, that which represents most accurately the true nature of rocks, is that which most resists fire, which melts [only] under an excessive heat, and finishes by vitrifying...

At the same time it is readily believed that at the origin of things before the separation of the opaque material from the luminous, when our globe was incandescent, the fire drove the humidity into the air, acting like a distillation. That is to say, as a result of the lowering of the temperature, it was converted into aqueous vapors. These vapors, finding themselves in contact with the chilled surface of the earth, condensed to water. The water, working over the debris of the recent conflagration, took up the fixed salts, giving rise to a sort of solution which soon formed the sea. . . —Gottfried Wilhelm Leibnitz (Protogaea, 1680; quoted in Boynton, 1948).

Precambrian geology (and Archean geology in particular) is the quintessential science of exiguous evidence. Ways must therefore be found to get around the gaps that - understandably enough - define the very earliest history of the Earth. This issue of Precambrian Research is the outcome of a special session (S44; New Views of Old Rocks) organized by S.J. Mojzsis (University of Colorado), Y. Ueno (Tokyo Institute of Technology) and T.M. Harrison (Australian National University) for the 13th V.M. Goldschmidt Geochemistry Conference that was held in Kurashiki, Japan 7-12 September, 2003. The range of topics covered in the session was diverse (see: www.ics-inc.co.jp/gold2003) yet devoted to a common theme: How can the first 20% of Earth history be understood, given the relative rarity (or outright absence) of a preserved rock record? Contributed papers to this special issue provide a glimpse of the expanding inventory of ancient crust revealed over the past decade and, moreover, serve as a natural complement to several recent issues of Precambrian Research including two devoted to "Archaean Tectonics" (vols. 127 in 2003 and 131 in 2004; edited by M.J. Van Kranendonk).

The five papers published here begin with three that explore the earliest hints of crust formation on Earth derived from (i) detailed studies of  $\leq$ 4.38 Ga detrital zircons in quartz-pebble conglomerates of the Jack Hills, Narryer Gneiss Complex of Western Australia, (ii) the origin and nature of diverse supracrustals and gneisses of the Itsaq Gneiss Complex of West Greenland, and (iii) the challenges posed by searching for evidence of extinct nuclides in the oldest rocks. The two subsequent papers describe the latest attempts to constrain seawater chemistry, atmospheric redox and crust/hydrosphere interactions from early Archean volcanosedimen-

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tary successions in the Pilbara and Barberton cratons.

Cavosie et al. present a thorough study of the geochemistry, age and origin of <4350 Ma detrital zircons from the Jack Hills, Narryer Gneiss Complex of Western Australia. It is generally agreed that during the first half-billion years following the accretion phase of the planets, geological processes on Earth were vigorous. However, no actual rocks older than ca. 4000 Ma thus far have been discovered (Bowring and Housh, 1995; Bowring and Williams, 2001) that can be used to directly evaluate this hypothesis. Tests of crustal growth models and the processes responsible for the destruction and recycling of new crust on the Hadean Earth whether by some form of fast and shallow plate tectonics (e.g. Martin, 1999) and plate foundering/stacking (Kroener, 1991), or the effects of bolide gardening (Sleep et al., 2001), have been stymied by a lack of analyzable material (DeWit and Ashwal, 1995), until now. Information has lately been provided as a result of the rejuvenation of interest in >4000 Ma detrital zircon grains from Western Australia. First discovered some two decades ago (Froude et al., 1983; Compston and Pidgeon, 1986), these "microrocks" preserve the only direct chemical evidence of early planetary crusts (Maas et al., 1992; Amelin et al., 1999). Cavosie et al. performed a combined ion microprobe, electron microprobe and electron micrography survey for this singular geological resource. They present data bearing on the geochronology, Th-U composition, zoning patterns revealed by cathodoluminescence (CL) imaging and inclusion mineralogy for a population of detrital zircons with <sup>207</sup>Pb/<sup>206</sup>Pb ages ranging from 4348-1576 Ma. The total range of zircon Th/U ratios extends from 0.04-7.5; zircons with 99-100% concordance have [Th/U]<sub>zircon</sub> restricted to 0.31-1.04 (Fig. 1). These values appear typical of those for igneous zircon populations (Mojzsis and Harrison, 2002). In support of this interpretation, Cavosie et al. point out that the majority of the zircons preserve what are likely primary growth features such as oscillatory and sector zoning revealed by CL imaging. The authors document mineral inclusions in the zircons suggestive of a granitoid parent (Maas and McCulloch, 1991; Maas et al., 1992), these observations coupled with previously reported oxygen isotope data for pre-4000 Ma zircons from this same site (Mojzsis et al., 2001; Valley et al., 2002) renders them much the same as contemporary zircons produced in common felsic magmas (Valley et al., 1994). Of the three criteria considered necessary for the establishment of a biosphere, the availability of organic raw materials, energy resources and liquid water, the last is the most difficult to satisfy except under special conditions on or within planetary crusts. The results of Cavosie et al. reinforce earlier conclusions that granitoid rocks and possibly continents and a hydrosphere were present on Earth since the earliest times, thus setting the stage for the appearance of life.

The most important sources of preserved pre-3600 Ma rocks on Earth are the Paleoarchean terranes of the Atlantic Province of the North American Craton (DeWit and Ashwal, 1995). Nutman et al. present a detailed description of the diversity of early Archean rocks and assess the potential for new discoveries in the  $\sim$ 3000 km<sup>2</sup> Itsag Gneiss Complex of West Greenland. In the area around Nuuk (Godthåb), high-grade gneisses have been studied and divided into two terranes based on differences in their pre-3600 Ma histories and tectonic emplacement, and separation from each other by younger rocks. Nutman et al. (1993, 1996, 2000, 2002) have termed these the Isukasia and Faeringehavn terranes based on the fact that in situ partial melts are absent in the Isukasia rocks. which also contain locally well-preserved  $\leq$  3810 Ma orthogneisses (metamorphosed tonalites) and some well-preserved early Archean volcanosedimentary sequences most notably in the Isua supracrustal belt. The *Faeringehavn* terrane appears to be different from the northeastern Isukasia rocks; it contains abundant 3.6-3.85 Ga migmatites with in situ partial melt dated to  $\sim$ 3.65 Ga. Within this terrane, Akilia (island) and nearby islets of the Ameralik region commonly contain ca. 3.83 Ga orthogneisses enclosing, and in some cases intruding, supracrustal units containing quartzites and banded iron-formation (Nutman et al., 1997). The importance of these rocks in interpreting the nature and timing of the establishment of a hydrosphere and life on Earth has generated much discussion in the last few years. Nutman et al. report on new work revealing that relatively low-strain domains and areas of limited anatexis exist on other islands near Akilia that likewise preserve  $\sim$  3850 Ma tonalitic orthogneisses. The geology of Akilia is neither unique nor unusual for rocks of this metamorphic grade and protolith, except in its antiquity. The paper contributes to our under-



Fig. 1. (A)  $[Th/U]_{zircon}$  vs. <sup>207</sup>Pb/<sup>206</sup>Pb plot for zircons from the Jack Hills, Narryer Gneiss Complex, Western Australia (data from Cavosie et al. this issue). (B) The grey region in the diagram shows the predicted range of magmatic  $[Th/U]_{zircon}$  values crystallizing from a melt of typical granitoid  $[Th/U]_{wr} = 4$ . Note that the plot of all data in (A) shows a wide scatter in Th/U; data in (B) are divided between >95% concordant spots (open circles) and those within 1% of concordance (closed squares). In this analysis, it can be seen that a significant population of the oldest zircons show evidence of an original magmatic parent (as opposed to metamorphic zircon growth; Mojzsis and Harrison, 2002).

standing of two newly discovered early Archean terranes north of the Nuuk region: the *Qarliit Tasersuat* assemblage and the *Aasivik* terrane. Both are smaller bodies than what comprise the *Itsaq Gneiss Complex* and consist of polyphase migmatitic gneisses up to  $\sim$ 3700 Ma in age and affected by early ( $\sim$ 3600 Ma) to late ( $\sim$ 2770–2550 Ma) Archean metamorphic events. Much interesting future work is anticipated as these ancient rocks become available for study to a wider group of researchers.

Sharma and Chen describe the challenges faced in searching for evidence of the extinct r-process nuclide (<sup>146</sup>Sm) previously reported from anomalous <sup>142</sup>Nd values in early Archean metasedimentary (Harper and Jacobsen, 1992) and metavolcanic rocks (Boyet et al., 2003). Attempts to document <sup>142</sup>Nd excesses with high

apparent  $\varepsilon_{Nd}^{143}$  in pre-3700 Ma rocks a dozen years ago (Harper and Jacobsen, 1992) yielded conflicting results (Sharma et al., 1996) that experienced an hiatus in advance of needed development of mass spectrometry technology and techniques of sample preparation. However, several recent studies meant to address the controversies (Caro et al., 2003; Papanastassiou et al. (2003)) appear to generate mutually exclusive results. Could the variable anomalies be the result of simple sample heterogeneity, data reduction effects, ion optics or some other phenomenon? Sharma and Chen argue that ion optical aberrations can probably be ruled out, and exponential (or Rayleigh) laws provide sufficient mass fractionation corrections without invoking second order corrections (cf. Cano et al., 2003). Analyses of enriched standards by Sharma and Chen confirm that a <sup>142</sup>Nd anomaly can be resolved at better than the +10 ppm level. They find that a sample aliquot of garnet-biotite schist from the Isua supracrustal belt with a history of <sup>142</sup>Nd measurements (IE 715-28; Jacobsen and Dymek, 1988; Harper and Jacobsen, 1992; Sharma et al., 1996) and likely representing a ferruginous metapelite (Mojzsis et al., 2003), has no resolvable <sup>142</sup>Nd anomaly from the nND- $\beta$  standard. The authors conclude that the absence of <sup>142</sup>Nd anomalies in their sample is an indication that the older crustal material with high initial  $\varepsilon_{\rm Nd}^{143}$  from which of IE 715-28 was derived points to highly depleted ( $f_{\text{Sm/Nd}} > 0.3$ ) reservoirs after  $\sim$ 4.25 Ga and that such reservoirs quickly became homogenized. Given the growing appreciation of the diversity of early Archean rocks in West Greenland (Nutman et al. this issue), and newly documented localities in for example the ca. 3.8 Ga Inukjuak Domain, Nuvvuagittuq Sequence in Canada (Stevenson et al., 2004), much material for analysis appears to be forthcoming.

Hayashi et al. explore the origin of early Archean sedimentary rocks from the Barberton Greenstone Belt in South Africa (ca. 3250 Ma) that carry negative Ce anomalies using La–Ce and Sm–Nd isotopic systematics coupled with light rare Earth element (LREE) abundances. The authors described negative Ce anomalies in two samples of a banded ferruginous chert and shale from Barberton with Ce/Ce<sup>\*</sup> values of 0.40 and 0.81, respectively. The ferruginous chert has a calculated initial Ce isotopic ratio  $^{138}$ Ce/<sup>142</sup>Ce (3250 Ma) = 0.0225059 far lower than both the CHUR value at 3250 Ma and the value at Earth formation,  $^{138}$ Ce/<sup>142</sup>Ce<sub>CHUR</sub>

(4560 Ma) = 0.0225409. Initial Ce isotope ratios for the anomalous shale sample are likewise lower than that of similar rocks where Ce anomalies are absent. Are the Ce anomalies inherited from some Archean redox change? The authors propose that later episodes of alteration are responsible for these unusual Ce values. By combining La, Nd and Sm geochemical data, La–Ce isotopic systematics may be used to place constraints on the time at which negative Ce anomalies were established in the rock. Knowing this, it might be possible to asses how REE data bear on the long sought-after question of how (whether, or to what degree) redox conditions in the Archean ocean changed over time.

Pillow basalts with intercalated dolomite from the Pilbara Block provide a potentially robust record of the REE composition of early Archean seawater. Yamamoto and co-authors test the hypothesis that chemical disturbances to the dolomite can be 'seen-through' because the Pilbara dolomites display chrondritenormalized LREE patterns with features characteristic of seawater. Because of the small Eu anomalies observed in the Pilbara dolomite, a significant hydrothermal contribution to the REE payload can probably be ruled out. Do the dolomites preserve REEs that can be used to deduce [REE]aq of Archean seawater? It may be possible to do this with useful carbonateseawater partition coefficients. Using new dolomite reference materials, Yamamoto et al. propose that [REE]<sub>aq</sub> was between one and two orders of magnitude greater in 3.4 Ga seawater compared to present and enriched in HREE. Such factors as higher salinity and bicarbonate concentration in the Archean oceans are held by the authors are reasons for the observed REE patterns.

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