

## Zircon Evidence of the Earliest Archean Crust: 4.0–4.4 Ga

JOHN W. VALLEY<sup>1</sup>, A.J. CAVOSIE<sup>1</sup>, C.M. GRAHAM<sup>2</sup>,  
E.M. KING<sup>1</sup>, W.H. PECK<sup>1</sup>, AND S.A. WILDE<sup>3</sup>

<sup>1</sup>Univ. of Wisconsin, Madison, WI 53706, USA  
(valley@geology.wisc.edu)

<sup>2</sup>Edinburgh Univ., Edinburgh, Scotland, EH9 3JW, U.K.

<sup>3</sup>Curtin Univ., Bentley, W. Australia, 6102, Australia

Detrital and xenocrystic zircons from 4 locations in the Yilgarn craton (W.A.) have U-Pb ages older than 4 Ga, the oldest is 4.404 Ga. These crystals are older than any dated terrestrial rock and provide our only solid evidence of the earliest Archean. The search for parent rocks is on-going (see Cavosie et al., this volume). Single crystals in one suite of detrital zircons from the Jack Hills metaconglomerate, including the oldest zircon, have been analyzed for age, (18O, and REEs by ion probe. Zircons are HREE enriched to 10,000x chondrite with positive Ce and negative Eu anomalies. Calculated magmas are LREE-enriched. CL imaging shows concentric growth zoning. Some zircons have correlated REE and (18O variation. The 4.4 Ga zircon measures  $\approx 100 \times 220$  (m and contains 1-20 (m inclusions of quartz and 0.4 – 1.0 (m inclusions that may be K-feldspar  $\pm$ qtz, albite, magnetite, and pyrite. Thus the parent magma was differentiated, quartz saturated and probably granitic (or rhyolitic), consistent with continental crust. Values of  $\delta^{18}\text{O}$  range from 5.0 to 7.4‰ VSMOW. This range in  $\delta^{18}\text{O}$  is the same as for younger zircons throughout the Archean, consistent with a similar genesis. Four crystals have  $\delta^{18}\text{O}$  higher than in mantle melts, suggesting crystallization in a magma formed by burial and melting of protoliths elevated in  $\delta^{18}\text{O}$  by interaction with low temperature fluids near the surface of the Earth (i.e., hydrothermal alteration, diagenesis, or weathering). While considerable uncertainty exists for many aspects of the early Archean, the best interpretation of these results is that liquid water existed on the surface of the Earth at least intermittently from 4.0-4.4 Ga. If the hydrosphere was similar to today, temperatures are indicated below 200°C (to elevate  $\delta^{18}\text{O}$  in protolith) with buffered atmospheric  $\text{P}(\text{H}_2\text{O})$ . Taken together, these results suggest rapid cooling of the Earth following accretion, and formation of the Moon and core. The flux of meteorite bombardment may have decreased more rapidly than previously thought permitting a “cool early Earth” from ca. 4.0 to 4.4 Ga. We are not aware of evidence to support or refute the evolution of life during this period, but if Earth experienced late heavy bombardment at ca. 3.9 Ga, then refugia for life existed only beneath the surface or in space.

## Carbocation reactions in sediments: The liquid reaction environment.

B.G.K. VAN AARSEN, T.P. BASTOW, R. ALEXANDER,  
R. I. KAGI

Centre for Petroleum and Environmental Organic

Geochemistry, Curtin University of Technology, Perth,

Western Australia (B.vanAarsen@curtin.edu.au)

The proportions of methylated naphthalenes in crude oils show relationships which are remarkably consistent in many different samples. Crude oils display constrained relations between the abundances of selected isomers, which are thought to be determined in the source rock before expulsion. For example, the ratios of three parameters, each based on the increase with maturity of stable isomers relative to less stable ones within a class of methylated naphthalenes, are linearly correlated to each other in crude oils. In contrast, in sediment extracts these relations are much less obvious. Similarly, the ratio of 1,3,6-TMN / 1,3,7-TMN shows a very narrow range of values in the oil set, but covers a much wider range in the sediments, although it appears to have an absolute minimum value.

To explain this behaviour of methylated naphthalenes it does not suffice to consider maturity and source effects. Therefore a new model is proposed involving a liquid reaction environment which is present in the source rock as an essential step in petroleum formation. The liquid reaction environment can be regarded as a liquid phase present in the source rock where it forms the medium for reactions that can take place between the many different organic compounds that are its constituents. It can be likened to a sedimentary reaction vessel, with its components forming both the solvent and the reactants. The reaction conditions within these liquids, of which temperature is the key factor, determine the composition of the petroleum before expulsion.

This model satisfactorily explains why the methylated naphthalenes display the relations as observed. Their distribution reflects the extent to which the system can take up input from the kerogen, and then redistribute the newly available methyl groups over the available naphthalene carbon skeletons. In contrast, when a sediment is extracted these compounds are mixed with methylated naphthalenes from other reaction environments present in the source rock, such as compounds adsorbed onto kerogen. This affects the total methylated naphthalenes distribution such that it no longer resembles that of a crude oil. The extent to which the liquid reaction environment has been established in the source rock can be gauged from the ratio of 1,3,6-TMN / 1,3,7-TMN. The closer this ratio in an extract is to that found in oils, the more the liquid reaction environment has contributed to the total extract.