# Diagenetic evolution of the Hooggenoeg Formation: Implication for Archean seawater composition

VIRGILE ROUCHON[1], BEATE ORBERGER[1], AXEL HOFMANN[2] AND DANIELE L. PINTI[3]

[1]Université Paris Sud, Laboratoire IDES UMR 8148, 91405 Orsay cedex, France. (virgile.rouchon@u-psud.fr)
[2]University of KwaZulu-Natal, Durban, South Africa
[3]UQAM-McGill-Geotop, Montreal, Canada

The reconstruction of the composition of the Archean atmosphere and ocean relies on scarce data and much theoretical modeling. We provide new constraints on this issue by studying the mineralogy and geochemistry of Archean sediments. The low-grade metamorphic Hooggenoeg Formation (HFm) of the Barberton greenstone belt is an extensive low-grade Paleoarchean volcano-sedimentary sequence, ideal for studying primitive diagenetic processes. The 3.45 Ga Upper HFm comprises a rhyodacitic volcanic complex with associated volcaniclastic sediments that locally overlie pillow basalts and hydrothermal orthochemical carbonaceous cherts. Detrital material was mainly derived from rhyodacites that were affected by an event of K-Si metasomatism prior to erosion. Phenocrysts, matrix and glass fragments were replaced by quartz-sericite-orthoclase and Ti-oxides still co-existing with primary apatite and zircon. After deposition, the detritus was cemented by early diagenetic microquartz. Silicification mainly resulted in $SiO_2$ dilution, as the trace element signatures (REE, HFSE) of the sedimentary source rocks were preserved.

Sandstones and conglomerates were affected by carbonatization (up to 40% vol.), as carbonate minerals replaced the diagenetic quartz cement and detritus. Three types of carbonate textures were sequentially formed: 1) Oscillatory zoned ankerite rhombs, 2) aggregates of ankerite-pyrite-sericite and 3) ankerite-calcite-albite-kaolinite. EPMA of carbonates revealed Na/Cl molar ratios of ~1 similar to seawater. The bulk $\delta^{13}C_{PDB}$ of carbonates ranges from +1.9 to +2.3 ‰, typical of a marine origin. The $\delta^{18}O_{SMOW}$ is homogeneous at +15 ‰, similar to deep-burial carbonates (120-160°C equilibrated with -2 ‰ < $\delta^{18}O_{SMOW}$ < +2 ‰ fluids). Regionally extensive seawater-basalt interaction zones that are developed below the sedimentary sequence provided large amounts of dissolved $SiO_2$, $Fe^{2+}$, $Ca^{2+}$ and $Mg^{2+}$. The $CO_2$-acidic (biologically unbuffered) ocean was in favorable conditions for early-diagenetic abiological silica cementation as opposed to carbonates. Trapped pore-fluids dissolved silicates as a result of temperature increase during burial. The related pH increase allowed carbonate precipitation at higher burial depth. This diagenetic evolution (silica→carbonates) is reversed compared to that observed in Phanerozoic sedimentary basins. Thermodynamic calculations will allow the determination of 3.45 Ga seawater-pH and related atmospheric $P_{CO2}$.

# CAIs in Rumuruti chondrites

S. S. ROUT AND A. BISCHOFF

Institut für Planetologie, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany (suryarout@uni-muenster.de)

Rumuruti chondrites (R-chondrites) are a group of chondritic meteorites that are highly oxidised, poor in metals, olivine rich (with high Fa content of ~39 mol%), and have high $\Delta^{17}O$ values. Barely any description of Al rich objects has been reported till now (Bischoff and Srinivasan, 2003; Berlin, 2003). Here, we present the results of our search and analysis of CAIs and Al-rich objects in the R-chondrites.

We studied 14 R-chondrites (NWA 753, 755, 1472, 1476, 1477, 1478, 3364, Rumuruti, Dhofar 1223, Acfer 217, Dar al Gani 013, Hughes 030, Hammadah al Hamra 119, and Sahara 99537) and found 102 Ca,Al-rich objects (87 CAIs, 13 Al-rich chondrules and 2 spinel-rich fragments). Based on the mineralogical characterisation by SEM and electron microprobe the inclusions can be grouped into seven classes:
(1) Concentric spinel-rich inclusions (30). These CAIs have abundant spinel and based on the presence or absence of major different phases can be subdivided into three groups:
(a) 18 CAIs dominantly consist of a spinel core rimmed by Al-rich diopside. (b) Five of the spinel-rich CAIs also contain abundant fassaite. These CAIs have a rim of diopside occasionally including olivine. (c) Within seven inclusions besides spinel abundant Na- and/or Cl-rich alteration products (probably nepheline and/or sodalite) were observed within the cores rimmed by diopside and, rarely, by olivine.
(2) One concentric hibonite-rich CAI has been found.
(3) Concentric fassaite-rich CAIs (3 spherules) have no rims and contain either hibonite or spinel and/or olivine and ilmenite as additional phases.
(4) Complex spinel-rich CAIs are the most abundant variety of CAIs (50): Based on their mineral abundances these CAIs can be subdivided into four other groups: (a) Two inclusions have also abundant hibonite. (b) 29 inclusions are rich in plagioclase (anorthite and/or oligoclase), and have sometimes fassaite. All the oligoclase-rich CAIs are devoid of any rims, but others generally have an Al-rich diopside rim. (c) 11 of the complex spinel-rich CAIs have major fassaite and Na- and/or Cl-rich alteration products mainly showing a complex mixture of spinel, fassaite, and alteration products. All CAIs have a diopsidic rim. (d) Complex spinel-rich CAIs with abundant Na-,Cl-rich alteration products (8) occasionally having a diopsidic rim.
(5) Three complex diopside-rimmed CAIs with minor fassaite and/or alteration products in the core and having a complex texture were found.
(6) 13 Al-rich chondrules were analysed.
(7) Two Al-rich (spinel-rich) fragments were found, whose relationship of these fragments to other types of inclusions described above is uncertain.

## References

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