

Identification of the oldest carotenoid breakdown products in the geological record

C. LEE^{1,2*} AND J.J. BROCKS¹

¹Research School of Earth Sciences, Australian National University, Canberra, Australia 0200

²Geological & Planetary Sciences, California Institute of Technology, Pasadena, CA 91125

(*correspondence: carinal@caltech.edu)

Carotenoids are often difficult to study in the geological record because of their low preservation potential. Preservation of the hydrocarbon equivalents of carotenoid molecules is rare due to their tendency to break into smaller units or undergo complex aromatisation and rearrangement reactions [1]. In rare instances where intact C₄₀ carotenoid hydrocarbons are preserved by suitable diagenetic conditions, they are often subsequently cleaved into smaller fragments by increasing temperatures during burial of the host sediment (catagenesis).

Upper sections of the 1.64 billion year old (Ga) Barney Creek Formation (BCF) in the McArthur Basin of northern Australia preserves more than 22 different C₄₀ carotenoid derivatives, including the hydrocarbons β -carotane, γ -carotane, and lycopane [2]. However, the C₄₀ structures disappear in deeper strata, although reasons for this disappearance were unknown. It could either be a result of diagenesis, increasing thermal maturity, or change in the biological source organisms.

We simulated the natural degradation of the carotenoid hydrocarbon, β -carotane, by way of hydrous pyrolysis. Hydrous pyrolysis of β -carotane generated a mixture of systematic thermal cleavage products that were used as a new elution standard [3].

We were able to successfully identify β -/ γ -carotane breakdown fragments even in deeper sections of the BCF. Given an intermittent disappearance and reappearance of these carotane fragments, as well as gradually declining concentrations with depth, we conclude that the combination of diagenesis and thermal maturity caused carotenoid decline. The fragments identified at 287 m depth in drill core GR-7 now represent the oldest evidence for non-aromatic carotenoids in the geological record.

[1] Koopmans *et al.* (1997) *Org. Geochem.* **26**(7-8) 451–466

[2] Brocks & Schaeffer, (2008) *Geochim. Cosmochim. Acta.* **72**, 1396–1414. [3] Lee & Brocks, (2011) *Org. Geochem. In Press*

Copper systematics in arc magmas and implications for the origin of continents, the Pb-paradox, and copper porphyry deposits

C.-T.A. LEE¹, E.J. CHIN¹, R. BOUCHET^{1,2}, P. LUFFI¹, R. DASGUPTA¹, D. MORTON³, V. LE ROUX⁴, Q.-Z. YIN⁵, F. ALBAREDE² AND J. Blichert-Toft²

¹Rice University, TX, USA (ctlee@rice.edu)

²Ecole Normale Supérieure, Lyon, France

³University of California, Riverside, CA, USA

⁴Woods Hole Oceanographic Institute, MA, USA

⁵University of California, Davis, CA, USA

Redox evolution during magma differentiation plays an important role in making continents, ore deposits, and the composition of the atmosphere. A powerful tracer of redox is S due to redox-sensitive speciation, but because S is easily disturbed by late-stage alteration, it is difficult to use as a robust tracer. However, Cu's unique affinity for sulfide makes it sensitive to S speciation and overall magma oxidation state. Here, we show that Cu in primitive arc and mid-ocean ridge basalts are similar and that the majority of arc magmas become depleted in Cu during differentiation. Thus, sulfide saturation and hence low oxygen fugacity generally characterize mantle melting and early magma differentiation in mid-ocean ridges and even most arcs. The fact that global continental crust is also depleted in Cu not only requires a missing Cu reservoir but also suggests that high oxygen fugacities are not critical in forming continental crust. We show that the missing Cu in arcs and continental crust is represented by sulfide-bearing pyroxenites formed as deep crustal cumulates that eventually founder into the mantle due to their high densities. Such foundering drives the residual crust towards felsic compositions and creates low U/Pb pyroxenite reservoirs in the deep mantle. Thus, the radiogenic Pb isotopic composition of the Earth's upper mantle is more likely attributed to continent formation than to protracted core formation. Instead of oxidized or metal-rich mantle sources, Cu-porphyrates probably derive from Cu-rich pyroxenites. These pyroxenites are most prone to re-melting during arc thickening, but because the pyroxenites are given to foundering, the window for Cu-porphyry formation is narrow. An important implication of this work is that subduction does not lead to efficient oxidation of the mantle. Therefore, oxygenation of the Earth's atmosphere is not controlled by evolution of mantle redox.