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## LA-ICP-MS elemental mapping of pyrite: An application to the Palaeoproterozoic atmosphere

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**Abstract:** A hydrothermal origin has been advocated for the genesis of rounded and subhedral-euhedral pyrite in some Neoarchaeon-Palaeoproterozoic clastic sedimentary rocks, thereby limiting their value as proxies for the composition of the early atmosphere. We present Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) element maps of rounded and euhedral-subhedral pyrite grains from the basal conglomerates of the Palaeoproterozoic Mississagi Formation, Huronian Supergroup, Canada. These maps reveal the common existence of rounded detrital cores and isolated grains variably modified by hydrothermal overgrowth. The detrital origin of pyrite grains is demonstrated by the rounding of isolated grains and the presence of cores in subhedral-euhedral grains. Rounding and breakage of grains is implied to have occurred via physical abrasion during sediment transport. Furthermore, trace element maps expose truncated cores of originally rounded detrital fragments that also indicate abrasive rather than accretional or dissolutional rounding. Finally, we document a complex core that consists of multiple grains suggestive of various source materials that were co-deposited in the original placer. Textural and geochemical evidence further suggests the detrital porous pyrite had a diagenetic origin prior to fluvial transport. Grain-size and shape analysis suggests that the large porous pyrite cores and grains may have had a shorter transport distance than the, on average, smaller compact rounded grains. Transport was prolonged from tributaries into the main valley, and the high energy setting implies well-aerated Palaeoproterozoic river water. Since pyrite is unstable under oxidising conditions, the frequent survival of detrital pyrite in the fluvial Mississagi Formation after sustained transport in the catchment basin and alluvial valley as well as aerated Palaeoproterozoic river waters therefore implies that the contemporary atmosphere was oxygen deficient. The depositional age of the Mississagi Formation is between 2.45 Ga (Thessalon Fm.) and 2.31 Ga (Gordon Lake Fm.), and the presence of the detrital pyrite therefore suggests that the atmosphere was devoid of any significant amount of free oxygen at the time immediately preceding the Great Oxygenation Event.

**Key words:** LA-ICP-MS; geochemical mapping; Palaeoproterozoic; atmosphere; pyrite

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