

## Applications of Raman XYZ mapping in the Earth sciences

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### Introduction

Raman spectroscopy is a powerful tool that has been applied widely in the earth sciences to characterize a variety of fluid and solid materials. While microspot Raman analyses have been used with great success to identify and characterize materials, it has previously been less useful for characterizing minor components in samples and for characterizing sample heterogeneities. The recent development of high-speed, high resolution mapping capabilities using the SWIFT™ (Scanning With Incredibly Fast Times)<sup>1</sup> apparatus now makes it possible to obtain high spectral, high spatial resolution Raman maps quickly and easily.

### Applications

One of the most successful applications of Raman spectroscopy in the earth sciences has been to analyze fluid (FI) and melt inclusions (MI). Many fluid phases that are common in FI, including H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>S, etc., are easily recognized and in some cases quantified using their Raman band intensities and/or positions. Recently, there has been much interest in searching for small amounts of H<sub>2</sub>O in FI that previously had been thought to contain only CO<sub>2</sub>. Confirming the presence of even small amounts of water in FI is important in understanding some upper mantle processes in which, as a result of exposure to high temperatures and pressures, hydrated minerals lose water that may then occupy FI. At room temperature the liquid H<sub>2</sub>O phase occurs as a thin, sub-microscopic rim on the walls of the inclusion, it has therefore been difficult, if not impossible, to locate the H<sub>2</sub>O film using spot analysis. Raman mapping, however, facilitates the search for H<sub>2</sub>O in these inclusions and provides a rapid method to survey large numbers of FI to see which, if any contain H<sub>2</sub>O.

Key to implementation of this method is the rapid mapping of many inclusions. This is achieved with SWIFT™ in which the sample is translated continuously and the detector readout is synchronized with that motion. Multivariate analysis methods are used to construct the Raman maps and indicate the presence, in this case, of the water. The same mapping technique has been used to examine the distribution of water in silicate melt inclusions, and to compare cathodoluminescence zones in zircon with the degree of metamictization of the sample based on Raman peak positions.

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## The Ediacarian Nitrogen Isotope Conundrum

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Nitrate cycling and isotope composition ( $\delta^{15}\text{N}$ ) in the oceans are strongly linked to the water column redox structure via its control on nitrogen speciation. The present-day nitrate  $\delta^{15}\text{N}$  in the oceans results from the balance between molecular nitrogen fixation, which yields nitrate close to 0‰, and water column denitrification which increases residual nitrate  $\delta^{15}\text{N}$  [1]. In upwelling zones, where disoxic conditions result in partial denitrification, residual nitrate  $\delta^{15}\text{N}$  are usually higher than +5‰. Since surface sediments most often record the  $\delta^{15}\text{N}$  of the nitrogen source used by primary producers and changes minimally during diagenesis, sediment  $\delta^{15}\text{N}$  can be used as a proxy for water column redox structure and nutrient influx [2]. During the Phanerozoic, sedimentary  $\delta^{15}\text{N}$  values typically cluster close to 5‰, except during ocean anoxic events (OAEs), when values are close to 0‰ [3]. These low  $\delta^{15}\text{N}$  values are attributed to a complete removal of fixed nitrogen species at the chemocline, which leaves nitrogen fixation as the dominant pathway of N assimilation.

The Ediacarian Period is expected to have seen a long-lived ocean redox stratification and the onset of deep ocean oxygenation. Hence significant variations in sedimentary  $\delta^{15}\text{N}$  values are to be expected in Ediacarian successions. Yet, hardly any  $\delta^{15}\text{N}$  data have been published so far for this period. We present preliminary  $\delta^{15}\text{N}$  data for 5 different Ediacarian platforms (South China, Svalbard, Canada, Brasil). Most of these platforms preserve separate evidence for redox stratification, but most of the data range between 3 and 6‰, with a few outliers reaching 1 or 9‰. These data suggest either a dominantly oxic Ediacaran ocean at odds with other proxies (geochemistry, sulfur isotopes and iron speciation), or an Ediacarian marine nitrogen cycle that operated very differently from Phanerozoic OAEs.

[1] Sigman et al. (2009) *Encyclopedia of Ocean Sciences*, 40-54.

[2] Galbraith et al (2008) *Nitrogen in the marine environment* **chap 34**, 1497-1526. [3] Meyers (2006) *Pal. Pal.* **235**, 305-320.