Femtosecond laser ablation ICP-MS: high repetition rate diode-pumped ytterbium performance

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Laser Ablation ICP-MS

Without doubt, the femtosecond laser offers compelling advantages to direct solid sample laser ablation (LA) chemical analysis with detection of elements and isotopes using ICP-MS. The femtosecond laser reduces matrix effects due to a nominal heat-affected zone (no fractionation) and provides a nanometer particle aerosol that is ideal for transport, vaporization and ionization in the ICP. Several groups have shown the benefits of femtosecond LA-ICP-MS, but there remains conflicting reports of the 'optimun' wavelength, energy and pulse duration for geological sample analysis. Fundamental studies have shown in many cases that these parameters are significantly relaxed once the pulse duration is less than approximately 1ps. Most of the previous fs-ablation applications have been demonstrated using Ti:Sapphire lasers. We demonstrated excellent performance for several geological samples using a smaller footprint, lower cost, and more reliable diode-pumped ytterbium femtosecond laser, even using wavelengths at 1um. Precision, sensitivity and accuracy were established and will be reported. In addition, the high repetition rate of this laser was demonstrated for rapid bulk analysis of inhomogeneous granite samples.

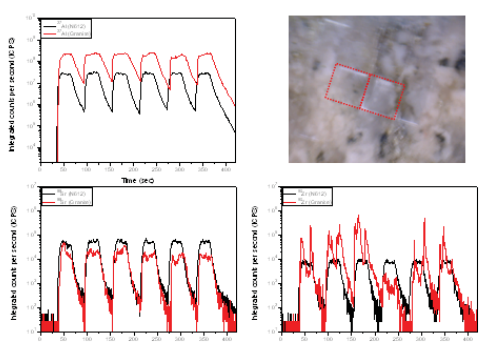

Figure 1: ICP-MS transient signal of selected isotopes produced by high repetition rate femtosecond laser ablation of NIST 612 and granite at 6um spot size, 40mm/sec and 20KHz. Scans show the effect of elemental inhomogeniety.

Conclusion

This talk will describe the current status of femtosecond laser abaltion ICP-MS with emphasis on the benefits of a reliable and stable diode pumped ytterbium solid state laser.

Novel synthesis of iron sulfide for carbon dioxide reduction

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Overview

Despite the high thermodynamic stability of CO_2, biological systems are capable of both activating and converting it into a range of organic molecules, under moderate conditions. Successful conversion of CO_2 into useful chemical intermediates without the need for extreme reaction conditions would be of enormous benefit Iron-nickel sulfide membranes formed in the warm, alkaline springs on the Archaean ocean floor are increasingly considered to be the early catalysts involved the emergence of life. These anaerobic reactions are thought to have been catalyzed by small (Fe,Ni)S clusters similar to the surfaces of present day sulfide minerals.[1]

We have synthesised iron sulfide nanomaterials using a novel synthesis methods based on continuous hydrothermal synthesis, where flows of aqueous solutions of iron and sulfide ions are brought into contact with a flow of superheated water (at 450 ºC). This results in sudden, rapid crystallisation of nanoparticle metal sulfides. A flow reactor such as this offers the potential to affect the particle properties, such as composition, based on modelled predictions of active catalysts. The conditions and processes occurring during synthesis can be compared to those that might occur in hydrothermal vents.[2,3] The electrochemical properties of these materials and their stability and activity towards CO_2 and their selectivity to products can be evaluated.

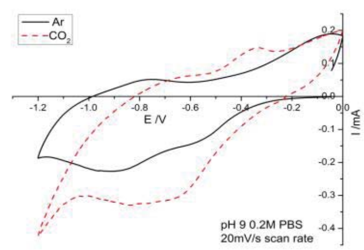

Figure 1: Comparison of the electrochemical behaviour of Ni-doped greigite under argon and CO_2.

Results

Based on comprehensive computational investigations, a number of iron and iron-nickel sulphide nanoparticles have been designed, synthesised, tested, characterised, and evaluated for the activation and chemical modification of CO_2 at low voltages (obtainable from solar energy). Succesful synthesis methods for greigite, mackinawite, pyrrhotite, pyrite and nickel sulfide as well as doped greigite nanostructures have been developed. Structures including nickel-doped greigite (above) show clear differences in electrochemical behaviour in the presence and absence of CO_2.

[1]Russell (2005) *Economic Geology* **100**, 419-438. [2]Crabtree (1997) *Science* **276**, 222-222. [3]Middelkoop (2009) *Chemistry of Materials* **21**, 2430-2435