

Laser ablation for spatially resolved radiocarbon measurements with gas source-accelerator mass spectrometry

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Accessing the spatial variability of ¹⁴C in solids like for example speleothems, corals or wood, traditionally required laborious and time consuming sample preparation (milling, drilling, graphitization) to allow measurements by accelerator mass spectrometry (AMS). With the availability of gas ion source AMS [1] and new sample preparation techniques and the direct measurement of gaseous carbon species (i.e. CO₂) a wider range of applications has become accessible. Laser ablation can directly produce CO₂ from carbonates at a spatial resolution of several 10 μm and is considered to complement currently available measurement strategies when high resolution radiocarbon records are of interest. In this study, a prototype laser ablation sampling unit is developed, which can be directly connected to the ion source of a gas-source AMS instrument. It comprises an ArF excimer laser (193 nm) with beam delivery optics, a specific ablation cell and sample observation system. Initial tests showed that using rectangular ablation crater of 100 μm x 700 μm can generate a sufficient CO₂ flux to allow radiocarbon measurements with the gas ion source AMS. The ablation cell was designed in order to avoid carry over effects of particulate debris from adjacent ablation spots and to ensure minimum signal dispersion at the operating conditions of the gas source AMS (i.e. 200 μL/min He as carrier gas). It consists of a volume-optimized gas expansion head with targeting and observation window and a large volume sub-unit capable of hosting sample specimen with sizes of up to 100 mm x 20 mm. The system configuration and initial results from ¹⁴C measurements will be discussed in this presentation.

[1] Ruff M. *et al*, A GAS ION SOURCE FOR RADIOCARBON MEASUREMENTS AT 200 kV, RADIOCARBON, Vol 49, Nr 2, 2007, p 307–314

SO₂ photoexcitation links polar sulfate and climate-impacting volcanism

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Natural climate variation, such as that caused by volcanoes, is the basis for identifying anthropogenic climate change. However, knowledge of the history of volcanic activity is inadequate, particularly concerning the explosivity of specific events. Some material is deposited in ice cores, but the concentration of glacial sulfate does not distinguish between tropospheric and stratospheric eruptions. Stable sulfur isotope abundances contain additional information, and recent studies show a correlation between volcanic plumes that reach the stratosphere and mass-independent anomalies in sulfur isotopes in glacial sulfate. We describe a mechanism, photoexcitation of SO₂, that links the two, yielding a useful metric of the explosivity of historic volcanic events. A plume model was constructed including photochemistry, entrainment of background air, and sulfate deposition. Isotopologue-specific photoexcitation rates were calculated based on the UV absorption cross-sections of ³²SO₂, ³³SO₂, ³⁴SO₂, and ³⁶SO₂ from 250 to 320 nm. The model shows that UV photoexcitation is enhanced with altitude, whereas mass-independent oxidation, such as SO₂ + OH, is suppressed by *in situ* plume chemistry, allowing the production and preservation of a mass-independent sulfur isotope anomaly in the sulfate product. We are able to identify the process controlling mass-independent sulfur isotope anomalies in the modern atmosphere. This mechanism is the basis of identifying the magnitude of historic volcanic events.