

Calibration of carbonate composition using micro-Raman analysis: Application to planetary surface exploration

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Laminated accretionary carbonate deposits, containing various amounts of kerogenous organic matter, are a prominent feature of this sedimentary record over the past 3,500 Myr. The macroscopic similarity to modern microbially-produced structures, has led to the inference that these structures may represent evidence of ancient life. Recently, Mg-Carbonates preserved in Martian dust were found by orbital-probe boarded IR spectrometry [1], but the analytical scale was too large to detect macroscopic carbonate structures of possible biologic origin. Raman micro-spectroscopy may offer an important innovation in planetary research, since it offers fast, high spatial resolution (μm) and in-situ identification of carbonates. Raman portability is also well-suited for planetary surface exploration.

Raman micro-spectrometry analysis was performed on a set of carbonate standards (calcite, ankerite, dolomite, siderite, magnesite) of known composition. Each carbonate Raman spectrum is characterized by six bands of different intensities and wave number. We show that Raman band shifts of siderite-magnesite and ankerite-dolomite solid solutions display a well defined positive correlation ($r^2 > 0.9$) with the Mg number ($\text{Mg}/(\text{Mg}+\text{Fe}+\text{Mn}+\text{Ca})$) of the carbonate analyzed. Raman shifts calibrated as a function of Mg number were used in turn to evaluate the chemical composition of carbonates. Raman analysis of a suite of carbonates (siderite, sidero-magnesite and ankerite) of hydrothermal and sedimentary origin from the 3.5 Gyr old Dresser Formation, Australia, show good compositional agreement with electron microprobe analysis. These results indicate that Raman spectrometry can provide crucial information on the composition and origin of carbonates on planetary surfaces.

[1] Banfield *et al.* (2003) *Science* **301**.

Arsenic remobilization from paddy soil during monsoon flooding in Bangladesh

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Groundwater containing high concentrations of arsenic (As) is extensively used for the irrigation of dry season rice in Bangladesh [1]. Though this enables Bangladesh to be self-sufficient in food, As accumulation in paddy soils may jeopardize rice production in the long term. Monsoon flooding strongly attenuates As accumulation in the topsoil of rice fields [2, 3], but the pathways of As release remain unclear. We present data from paddy fields near Sreenagar (Munshiganj, Bangladesh) which show that As was reductively mobilized and released into the overlying floodwater throughout the duration of monsoon flooding. As concentrations in topsoil porewater increased over time, reaching values of up to $1160 \mu\text{g L}^{-1}$ at 3-7 cm depth after 16 weeks of flooding. The floodwater column was either vertically well mixed exhibiting As concentrations between 5 and $20 \mu\text{g L}^{-1}$ over a height of 1-2.7 m, or characterized by distinct gradients of increasing As concentrations towards the soil surface. On days of limited vertical mixing, As concentrations ranged between $40\text{-}120 \mu\text{g L}^{-1}$ in floodwater 2.5 cm above the soil. Using different methods we estimate that between 53 and 250 mg m^{-2} of As, corresponding to 13-63% of the As annually added via irrigation, were mobilized into floodwater over the course of one monsoon season. A large portion of this arsenic is likely to be exported through the river system draining Bangladesh to the Bay of Bengal.

[1] Ali *et al.* (2003) In *Fate of As in the environment*, ITN: Dhaka, 7-20. [2] Dittmar *et al.* (2007) *ES&T* **41**, 5967-5972. [3] Saha & Ali (2007) *Sci. Total Environ.* **379**, 180-189.