Atmospheric trace gases and isotopologues using mid-IR laser direct absorption spectroscopy

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Recent advances in mid-infrared laser technology have greatly facilitated field measurements of atmospheric trace gases to identify and quantify their sources and sinks. Newly available non-cryogenic mid-infrared lasers and detectors, long path length, small volume sampling cells, and advances in direct absorption techniques with have led to smaller, lighter, and more robust instrumentation for measurements from mobile and aircraft platforms, field sites at remote locations, and laboratories for clumped isotopologues. The reliability and reproducibility of the mid-infrared lasers has led to long term monitoring and turn-key operation. Trace gas detection in ambient air at the low part-per-trillion levels are now feasible. Fractional precisions of less than 1 part in 10,000 allow for isotopologue ratio measurements of carbon dioxide, methane, and nitrous oxide at atmospheric mixing ratio levels. Applications to measurements of greenhouse gas emissions of methane and nitrous oxide, high precision measurements of carbonyl sulphide (OCS), measurements of ethane (C_2H_6) to determine sources of methane, and isotopologue measurements of CO_2, CH_4, N_2O and H_2O, will be presented.

TRACE GASES *ambient mixing ratios*	**Frequency** cm^{-1}	*1 s std dev [ppt]* *210 m*	*76 m*
CH_4	1275	100	300
$^{13}CH_4/CH_4$	1294	1.5‰	
OCS	2050	2	5
CO	2199		40
N_2O	2199		20
$^{15}N^{14}NO$, $^{14}N^{15}NO$	2188	3‰	
$^{13}CO_2$, $C^{18}O^{16}O$	2311		0.1‰
C_2H_6	2996		20
$^{13}CH_4/CH_4$	3057	0.5‰	
CH_3D/CH_4	3060	20‰	

Impacts and LIPs: $^{187}Os/^{188}Os$ signatures across the K-Pg boundary

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Both impacts and large igneous provinces (LIPs) can introduce unradiogneic Os into the global ocean producing excursions to lower $^{187}Os/^{188}Os$ in pelagic sediments. The $^{187}Os/^{188}Os$ excursion caused by the late Eocene Popigai impact is consistent with abrupt addition of soluble meteoritic Os to the ocean [1]. In contrast, previously reported $^{187}Os/^{188}Os$ excursions related to LIPs show greater variability and longer duration than the Popigai Os excursion. It is well established that the Chicxulub impact event is coincident with the K-Pg mass extinction and that eruption of the Deccan Traps began before, and continued after, the extinction event. Comparison of the Popigai excursion to the Cretaceous-Paleogene (K-Pg) boundary $^{187}Os/^{188}Os$ record provides a means of assessing whether or not eruption of the Deccan liberated significant amounts of mantle-derived Os to the ocean-atmosphere system coincident with the K-Pg mass extinction. In the Equatorial Pacific, South Atlantic and Atlantic-sector of the Southern Ocean the recovery of the marine $^{187}Os/^{188}Os$ record to higher pre-extinction levels [2] closely resembles the shape and duration of the Os recovery from the Popigai impact event. This similarity does not support claims [3] that the main phase of the Deccan volcanism is closely linked to the K-Pg mass extinction. However, an Indian Ocean site (ODP 738C) on the Keguelen Plateau displays $^{187}Os/^{188}Os$ ratios consistantly below those from other ocean basins during the Paleogene. In close proximity to the K-Pg boundary in ODP 738C, the Os-Ir-$^{187}Os/^{188}Os$ siganture is unequivoally meteoritic. Upsection, low $^{187}Os/^{188}Os$ ratios as far as 4.5m above the boundary (≈ 1.2 M.Y.) are unlikely to be related to the Chicxulub impact event. These low $^{187}Os/^{188}Os$ ratios in the Indian Ocean may be fingerprint of Paleogene LIP activity associated with either the Deccan or Kerguelen, but other interpretations are possible. The marine $^{187}Os/^{188}Os$ record allows large impact events to be differentiated from the emplacement of LIPs, and may preserve regional gradients in seawater $^{187}Os/^{188}Os$ controlled by the proximity to active volcanism.

[1] Paquay *et al*. (2008) Science 320, 214-218. [2] Ravizza and Vonderhaar (2012) Paleoceanography 27, 10.1029/2012PA002301. [3] Keller *et al*. (2009) EPSL 282, 10-23.

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