Development of a spectroscopic integrated system for remote and continuous monitoring of volcanic gases

Scientific Coordinator
Name-Position Paolo De Natale, Research Director

Affiliation Istituto Nazionale di Ottica Applicata (INOA)

ACTIVITY REPORT –2nd YEAR

PROJECT PARTICIPANTS

RU1	Istituto Nazionale di Ottica Applicata	Paolo De Natale
RU2	Dipartimento di Scienze Ambientali	Livio Gianfrani
RU3	Cambridge University	Clive Oppenheimer
RU4	Rice University	Frank K. Tittel

GENERAL OBJECTIVES

- Joint field campaigns at Solfatara, Vulcano island and Mt. Etna: Testing of the spectrometers at volcanic sites.
- Upgrading and modifications of the spectrometers based on the results of the field campaigns.

TASK 1 - FIELD CAMPAIGNS

- RU1, RU2, RU3
- Joint field campaigns at Solfatara, Vulcano island and Mt. Etna: Testing of the spectrometers at volcanic sites

- 2nd YEAR RESULTS

As shown in each research unit report, the scheduled joint campaign was performed in July 2002.
Scientists from RU1, RU2, and RU3 took data at Solfatara on the 16th July, and from 22nd to 26th at Vulcano Island. Different measurement methodologies were used in these occasions. RU1 and RU2 deployed the Portable Diode Laser Spectrometer, in an open-path configuration, to measure CO_2 and H_2O concentrations in different locations of both sites. System control and continuous data acquisition was carried out using a program written under LabView platform. Concentrations up to 3300(100)ppm and 74000(1000)ppm for CO_2 and H_2O, respectively, were measured at Solfatara.
RU3 used the UV spectroscopic system already described in the scientific report of Year 1. SO_2 fluxes at Vulcano, Stromboli and Mt. Etna (averages of 14, 280 and 940 Mg d^{-1}, respectively) were measured . Unlike the conventional approach of traversing underneath the plume, this technique can be operated from fixed positions, providing higher (every few minutes) time resolution data. Side-by-side measurements for Etna with a COSPEC operated by a INGV group from Catania, providing an important intercomparison of the old and new methods (Figure 2), were also performed.
After a careful analysis of the peculiar technical problems due to the site, evidenced in the fieldwork of the three other RU, the portable modular gas sensor for measuring the 13C/12C isotopic ratio in CO_2, developed by RU4, was considered to be not ready and robust enough for field work at Solfatara with the INOA, DSA and CU groups.

TASK 2 - UPGRADES OF THE OPTICAL SPECTROMETERS

- RU2, RU4
- Upgrading and modifications of the spectrometers based on the results of the field campaigns

- 2nd YEAR RESULTS

Most of the efforts of RU2 were devoted to the development of a novel method for $^{13}CO_2/^{12}CO_2$ isotope ratio measurements, based on diode laser spectroscopy. A compact and portable spectrometer has been implemented, in close collaboration with RU1, operating with a room-temperature DFB diode laser at the unusual wavelength of 2.007

micron. As a result of the accurate measurements of the absolute intensity for a large number of CO_2 lines, optimum $^{13}CO_2$ and $^{12}CO_2$ line pairs were selected. A BASIC code was developed for system control and continuous data acquisition, while spectra analysis and retrieval of the isotope ratio were carried out through a MATLAB code. A large variety of laboratory tests have been performed to determine the precision levels in the super-ratio determination. Earlier tests were performed using pure CO_2 samples, in a low pressure regime (about 1 Torr), and 3rd harmonic detection of the absorption signals. In this case, a 1‰-precision was found (absolute statistical uncertainty corresponding to one standard deviation, over 30 repeated measurements) in both the short (over few hours) and long (over several days) terms. The situation drastically changed when using CO_2-N_2 mixtures at a total pressure of about 100 Torr. Indeed, although the absorption signals were reduced, the much wider lines observed enabled to improve the horizontal resolution, i.e. the number of acquired points for each line profile. Hence, the precision level was improved, using a 2 % mixture, up to a level of 0.2 ‰.

RU4 has developed a system for $^{13}CO_2/^{12}CO_2$ isotopic ratio measurements that makes use of a difference frequency-based sensor operating around 4.35 microns (~2300 cm^{-1}). A portable modular gas sensor for measuring the 13C/12C isotopic ratio in CO_2 present in volcanic emissions with a precision of $1^0/_{00}$ was completed. The main limitation factors of the system during laboratory tests were inherent detector noise and imperfect N_2 purging of the open path part of the sensor. These error sources can be significantly reduced by increasing the difference frequency generation (DFG) power, that is feasible with present technology of fiber amplifiers.

Another approach under development by RU4 is to utilize a less complex and more compact spectroscopic source (a thermoelectrically cooled, pulsed quantum cascade laser operating in a single frequency mode at 4.35 microns). For this reason an order of such a laser was placed from Alpes Lasers in Neuchatel, Switzerland., the only commercial source to date for such lasers. Although to-date Alpes has not been able to fabricate and deliver such a laser, it is expected at the beginning of 2003 and the rest of the set-up has already been built. This laser can be current and temperature tuned to two optimum $^{13}CO_2$ and $^{12}CO_2$ absorption lines at 2311 cm^{-1} in order to measure changes in ^{13}del with a precision of $0.1^0/_{00}$ This precision value, together with the similar result achieved with the DFB diode laser spectrometer, could represent a breakthrough for continuous acquisition of isotopic ratio measurements in volcanic sites, though careful field testing will be necessary during year III of the Project.

On the basis of the field experiences acquired during the II year of activity, we plan to make other joint field campaigns during the II year, deploying improved and better suited instrumentation, with the aim to state the final levels of performance of each instrument as well as to define the combined data acquisition capabilities when all of them are deployed.

- RESEARCH PRODUCTS OF THE PROJECT
  - n° of articles published on international journals=**28**
  - n° of articles published on national journals, proceedings, technical reports=**2**
  - invited papers and talks=**1**
  - Presentations at international meetings=**3**
  - Presentations at national meetings=**4**
  - Data base
  - Computation codes=**2**
  - Other

PUBLICATIONS LIST (inclusive of papers in prints and accepted)

Oppenheimer, C., Pyle, D., and Barclay, J. (editors), 2003, *Volcanic degassing*, Special Publication, Geological Society of London, in press for February 2003.

Oppenheimer, C., 2003, Volcanic degassing, *Treatise on Geochemistry*, Volume 3, Chapter 6, Elsevier, in press.

Allen, A.G., Oppenheimer, C., Ferm, M., Baxter, P.J., Horrocks, L., Galle, B., McGonigle, A.J.S., and Duffell, H.J., Primary sulphate aerosol and associated emissions from Masaya volcano, Nicaragua, *Journal of Geophysical Research-Atmospheres*, in press.

Burton, M., Allard, P., Murè, F., and Oppenheimer, C., FTIR remote sensing of fractional magma degassing at Mt. Etna, Sicily, in *Volcanic degassing*, Geological Society Special Publication, in press.

Edmonds, M., Oppenheimer, C., Pyle, D.M., Herd, R., Rainwater and ash leachate analysis as a proxy for plume chemistry at Soufrière Hills Volcano, Montserrat, in *Volcanic degassing*, Geological Society Special Publication, in press.

Richter, D., Erdelyi, M., Curl, R.F., Tittel, F.K., Oppenheimer, C., Duffell, H.J., and Burton, M., 2002, Field measurement of volcanic gases using tunable diode laser based mid-infrared and Fourier transform infrared spectrometers, *Optics and Lasers in Engineering*, 37, 171-186.

Horrocks, L., Oppenheimer, C., Burton, M., Duffell, H., Compositional variation in tropospheric volcanic gas plumes: evidence from ground-based remote sensing, in *Volcanic degassing*, Geological Society Special Publication, in press.

McGonigle, A.J.S., & Oppenheimer, C., Optical sensing of volcanic gas and aerosol emissions, in *Volcanic degassing*, Geological Society Special Publication, in press.

McGonigle A.J.S., Oppenheimer C., Galle B., Mather T. and Pyle D., Walking traverse and scanning DOAS measurements of volcanic gas emission rates, *Geophysical Research Letters*, DOI 10.1029/2002GL015827, 26 October 2002.

Porter, J.N., Horton, K., Mouginis-Mark, P., Lienert, B., Lau, E., Sutton, A.J., Elias, T., and Oppenheimer, C., 2002, Sun photometer and lidar measurements of the plume from the Hawaii Kilauea volcano Pu'u 'O'o vent: estimates of aerosol flux rates and SO_2 lifetime, *Geophysical Research Letters*, DOI 10.1029/2002GL014744, 23 August 2002.

Galle, B., Oppenheimer, C., Geyer, A., McGonigle, A., Edmonds, M., and Horrocks, L.A., 2002, A miniaturised ultraviolet spectrometer for remote sensing of SO_2 fluxes: a new tool for volcano surveillance, *Journal of Volcanology and Geothermal Research*, 119, 241-254.

Oppenheimer, C., Burton, M.R., Durieux, J., and Pyle, D.M., 2002, Open-path Fourier transform spectroscopy of gas emissions from a carbonatite volcano: Oldoinyo Lengai, Tanzania, *Optics and Lasers in Engineering*, 37, 203-214.

Oppenheimer, C., Edmonds, M., Francis, P., and Burton, M.R., 2002, Variation in HCl/SO_2 gas ratios observed by Fourier transform spectroscopy at Soufrière Hills Volcano, Montserrat, in Druitt, T.H., and Kokelaar, P. (eds) *The eruption of Soufrière Hills Volcano, Montserrat, from 1995 to 1999*. Geological Society, London, Memoir, 21, 621-639.

Edmonds, M., Pyle, D., and Oppenheimer, C., 2002, HCl emissions at Soufrière Hills Volcano, Montserrat, West Indies, during the second phase of dome-building: November 1999 to October 2000, *Bulletin of Volcanology*, 64, 21-30.

G. Gagliardi, S. Viciani, M. Inguscio, P. De Natale, C. Gmachl, F. Capasso, D.L. Sivco, J.N. Baillargeon, A.L. Hutchinson, A.Y. Cho "Generation of tunable far-infrared radiation using a quantum cascade laser" *Optics Letters*, **27**, 521-523 (2002).

D. Mazzotti, S. Borri, P. Cancio, G. Giusfredi, P. De Natale "Low-power Lamb-dip spectroscopy of very weak CO_2 transitions around 4.25 μm" *Optics Letters*, **27**, 1256-1258 (2002).

G. Gagliardi, F. Tamassia, P. De Natale, C. Gmachl, F. Capasso, D.L. Sivco, J.N.Baillargeon, A.L. Hutchinson, A.Y. Cho "Sensitive detection of methane and nitrous oxide isotopomers using a continuous wave quantum cascade laser" *European Physical Journal D* **19**, 327-331 (2002).

S. Borri, P. Cancio, G. Giusfredi, D. Mazzotti, P. De Natale "Difference-Frequency Generation as a Precise Tool for High Resolution Spectroscopy" SPIE Proceedings, in press (submitted 6/2002).

G. Gagliardi, R. Restieri, G. Casa, and L. Gianfrani: "Chemical and isotopic analysis using diode laser spectroscopy: applications to volcanic gas monitoring", Opt. & Las. Eng. 37, 131-142 (2002).

A.Rocco, G.De Natale, P.De Natale, G.Gagliardi, L.Gianfrani"A diode-laser-based spectrometer for in-situ measurement of volcanic gases", Appl. Phys. B, submitted.

A. Rocco, G. Battipaglia, A. Castrillo, G. Gagliardi, A. Peressotti, M.F. Cotrufo, and L. Gianfrani: "Assessing soil respiration by means of near-infrared diode laser spectroscopy", Env. Sci. & Tech., submitted.

P. De Natale Recent advances in infrared sources for high resolution spectroscopy, *Seventeenth Colloquium on High Resolution Molecular Spectroscopy*, Papendal (Netherlands), Settembre, 9-13 2001. p.247 Programme and Abstracts (Invited lecture).

G. Gagliardi, P. De Natale, S. Viciani, M. Inguscio, C. Gmachl, F. Capasso, D.L. Sivco, J.N. Baillargeon, A.L. Hutchinson, and A.Y. Cho FIR generation and mid-IR spectroscopy using an 8-micron cw Quantum Cascade laser, Proceedings *3rd International Conference on "Tunable Diode Laser Spectroscopy" TDLS - 2001*, Zermatt, Switzerland, 8-12 July 2001.

G. Gagliardi, S. Viciani, M. Inguscio, P. De Natale, F. Tamassia, C. Gmachl, F. Capasso, D.L. Sivco, J.N. Baillargeon, A.L. Hutchinson, A.Y. Cho "Mid and far-infrared spectroscopy using a CW Quantum Cascade Laser"*17th International Conference on High Resolution Molecular Spectroscopy*, Praga, Repubblica Ceca, 1-5/9/2002.

A. Castrillo, G. Gagliardi, G. Casa, and L. Gianfrani: "Solving the problem of the accurate determination of absolute line intensities in molecular spectra", Phys. Rev. A, submitted.

E.R.Th. Kerstel, G. Gagliardi, L. Gianfrani, H.A.J. Meijer, R. van Trigt, and R. Ramaker: "Determination of the $^{2}H/^{1}H$, $^{17}O/^{16}O$, and $^{18}O/^{16}O$ isotope ratios in water by means of tunable diode laser spectroscopy at 1.39 μm", Spectr. Acta A58, 2389-2396 (2002).

G. Gagliardi and L. Gianfrani: "Trace-gas analysis using diode lasers in the near-IR and long-path techniques", Opt. Las. Eng. 37, 509-520 (2002).

G. Gagliardi, E. R. Th. Kerstel, and L. Gianfrani: "Isotope analysis in atmospheric relevant molecules by means of diode laser spectroscopy", INFMeeting, Annual Meeting of the National Institute for Matter Physics", Bari, 24-28 June 2002.

A. Castrillo, G. Gagliardi and L. Gianfrani: "Interferometry and absorption spectroscopy for absolute line intensity measurements of carbon dioxide around 2 micron", INFMeeting, Annual Meeting of the National Institute for Matter Physics", Bari, 24-28 June 2002.

G. Gagliardi, A. Castrillo, and L. Gianfrani: "Absolute line intensity measurements for carbon dioxide around 2 micron using interferometry and absorption spectroscopy", 17th International Conference on High Resolution Molecular Spectroscopy, Praga, 1-5 Sept. 2002.

A. Rocco, G. Battipaglia, G. Gagliardi, A. Peressotti, M.F. Cotrufo, and L. Gianfrani: "Studio delle emissioni naturali di CO_2 da parte di suoli mediante spettroscopia laser nel vicino infrarosso", LXXXVIII National Congress of the Italian Physics Society, Alghero, 26 Sept. - 1 Oct. 2002.

G. Battipaglia, A. Rocco, G. Gagliardi, A. Peressotti, L. Gianfrani, M.F. Cotrufo, "Nuove prospettive per misure di flussi di CO_2 fra suolo e atmosfera in sistemi dinamici chiusi", National Congress of the Italian Society of Ecology, Urbino, 16- 19 Sept. 2002.

D.Mazzotti, G.Giusfredi, P.Cancio, P.De Natale "High-sensitivity spectroscopy of CO2 around 4.25 mm with difference-frequency radiation", Opt. & Las. Eng. 37, 143-158 (2002).

P.Ferraro, G.De Natale "On the possible use of optical fiber Bragg gratings as strain sensors for geodynamical monitoring", Opt. & Las. Eng. 37, 115-130 (2002).

M. Erdelyi, D. Richter and F.K. Tittel, "$^{13}CO_2/^{12}CO_2$ isotopic ratio measurements using a difference based sensor operating at 4.35 microns", Applied Physics **B75**, 351-357 (2002).

D. Richter, A. Fried, B.P. Wert, J.G. Walega, and F.K. Tittel, "Development of a tunable mid-IR difference laser source for highly sensitive airborne trace gas detection", Applied Physics **B75**, 281-288 (2002)

A,A Kosterev, R.F.Curl, F.K.Tittel, R.Koehler,C.Gmachl, F.Capasso, D.L.Sivco, A.Y Cho, S. Wehe and M. Allen, Room Temperature quantum cascade laser based gas sensor for continuous monitoring of atmospheric CO", Applied Optics **41**, 1169-1173 (2002)

M.Erdelyi,R.F.Curl and F.K.Tittel, "Portable diode laser based sensor for $^{13}CO_2/^{12}CO_2$ isotopic ratio measurements" Optical Society of America Annual Meeting, Long Beach, CA (Oct 14-18, 2001)

Development of a spectroscopic integrated system for remote and continuous monitoring of volcanic gases.

RU Responsible
Name-Position: Paolo De Natale, Research Director
Affiliation: Istituto Nazionale di Ottica Applicata (INOA)

ACTIVITY REPORT–2nd YEAR

RU PARTICIPANTS

Name-Position	Affiliation	man/month
Dr. Paolo De Natale	INOA	2
Dr. Giuseppe De Natale , Research Director	OV	2
Dr. Alessandra Rocco Post-Doc fellowship	INOA	10
Roberto Abbate (Technician)	INOA	1
Dr. Pablo Cancio Post-doc fellowship	INOA	2
Paolo Bianchi (optical technician)	INOA	1

- **2nd YEAR OBJECTIVES**
  - Joint field campaigns at Solfatara, Vulcano island and Mt. Etna: Testing of the spectrometers at volcanic sites.
  - Upgrading and modifications of the spectrometers based on the results of the field campaigns.

- 2nd YEAR RESULTS **(max 1 page)**

The second year activity of the project was mainly devoted to the improvement of the DLS spectrometer, especially concerning its use in field campaigns. Many test measurements were carried out at Solfatara Volcano, while a joint field campaign in collaboration with the Cambridge University Group was successfully performed in July 2002 both at Solfatara and at Vulcano Island.
The upgrading of the DLS involved both the acquisition technique and the optical layout. The acquisition system was switched to a combination of a portable, battery operated, oscilloscope, and a laptop computer to perform continuous data acquisition. To this aim a new program was developed, in collaboration with the DSA, which utilises the LabView© platform. The maximum acquisition rate is $1sec^{-1}$ ("sample" mode,, of the oscilloscope) but it was fixed to $0.2sec^{-1}$ because the "average" acquisition mode increases the digital resolution of the oscilloscope. At present, up to 999 spectra can be continuously acquired.

The optical modifications of the spectrometer involved both the use of a portable breadboard where the 2μm diode laser system was mounted, and the implementation, to perform open-path measurements, of the Herriott multiple reflection cell especially designed for our system. The building materials for the cell, having an optical path length of approximately 20m, are stainless steel (316) for the body and gold for coating the spherical glass mirrors. In fact, the cell must withstand the particularly aggressive chemical compounds formed in volcanic emissions.

Figure 1: Experimental configuration of the PDLS.

The new design, shown in fig.1 was deployed during the July 2002 field campaigns.
Using the DLS spectrometer, in-situ H_2O and CO_2 concentration measurements were taken, vs. time. Examples of the retrieved values vs. time are reported in fig.2, where measurements taken at Solfatara crater are shown. The total observation time was approx. 900sec. The detection bench with the cell was positioned at a distance of approx. 1.5m from the fumarole, and at an height of 0.2m with respect to the ground.
The concentrations were retrieved from the acquired spectra by means of a non linear least-square fitting developed in a Matlab© environment. Data analysis required particular care in order to separate the contribution caused by background signal variations (due to change in the environmental conditions as well as wind, which caused oscillation of the optical fibres) from the variations in the concentrations of the molecules under analysis. The whole fitting procedure (robustness and accuracy) was deeply tested.

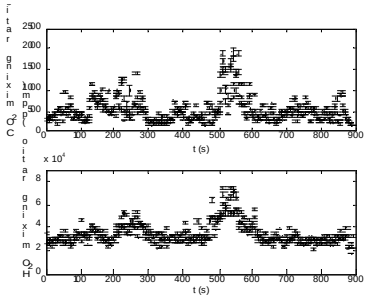
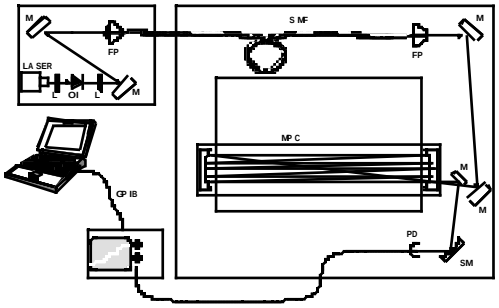


Figure 2 : CO_2 and H_2O concentrations vs. time, recorded at Solfatara Volcano on July, 16th 2002.

Both field campaigns provided extremely useful information on the system. In particular, the field tests suggested modifications to the set-up, in order to increase its efficiency as well as its performances. As for the spectrometer building materials, stainless steel resulted to be very well suited for the Solfatara environment but still partly prone to chemical aggression when deployed on top of Fossa Grande crater, at Vulcano.



- RESEARCH PRODUCTS
  - Scientific publications:
    - 5 published in international journals
    - 1 accepted
    - 2 submitted
  - Conference presentations
    - 1 Invited talk
    - 2 oral presentations
    - 1 poster presentation
  - New geochemical data
  - Field-tested spectrometers

PUBLICATIONS LIST

D.Mazzotti, G.Giusfredi, P.Cancio, P.De Natale "High-sensitivity spectroscopy of CO_2 around 4.25 μm with difference-frequency radiation", Opt. & Las. Eng. 37, 143-158 (2002).

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"Generation of tunable far-infrared radiation using a quantum cascade laser"
Optics Letters, **27**, 521-523 (2002).

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European Physical Journal D, **19**, 327-331 (2002).

S. Borri, P. Cancio, G. Giusfredi, D. Mazzotti, P. De Natale "Difference-Frequency Generation as a Precise Tool for High Resolution Spectroscopy"
SPIE Proceedings, in press (sumitted 6/2002).

A.Rocco, G.De Natale, P.De Natale, G.Gagliardi, L.Gianfrani "A diode-laser-based spectrometer for in-situ measurement of volcanic gases", Appl. Phys. B, submitted.

A. Rocco, G. Battipaglia, A. Castrillo, G. Gagliardi, A. Peressotti, M.F. Cotrufo, and L. Gianfrani: "Assessing soil respiration by means of near-infrared diode laser spectroscopy", Env. Sci. & Tech., submitted.

CONFERENCE PRESENTATIONS

P. De Natale, "Recent advances in infrared sources for high resolution spectroscopy"

Seventeenth Colloquium on High Resolution Molecular Spectroscopy, Papendal (Netherlands), Settembre, 9-13 2001. p.247 Programme and Abstracts (Invited lecture).

G. Gagliardi, P. De Natale, S. Viciani, M. Inguscio, C. Gmachl, F. Capasso, D.L. Sivco, J.N. Baillargeon, A.L. Hutchinson, and A.Y. Cho "FIR generation and mid-IR spectroscopy using an 8-micron cw Quantum Cascade laser"
Proceedings *3rd International Conference on "Tunable Diode Laser Spectroscopy" TDLS - 2001*, Zermatt, Switzerland, 8-12 July 2001.

G. Gagliardi, S. Viciani, M. Inguscio, P. De Natale, F. Tamassia, C. Gmachl, F. Capasso, D.L. Sivco, J.N. Baillargeon, A.L. Hutchinson, A.Y. Cho „Mid and far-infrared spectroscopy using a CW Quantum Cascade Laser"
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A. Rocco, G. Battipaglia, G. Gagliardi, A. Peressotti, M.F. Cotrufo, and L. Gianfrani: "Studio delle emissioni naturali di CO_2 da parte di suoli mediante spettroscopia laser nel vicino infrarosso", LXXXVIII National Congress of the Italian Physics Society, Alghero, 26 Sept. - 1 Oct. 2002.

Project title:
Development of a spectroscopic integrated system for remote and continuous monitoring of volcanic gases.

RU responsible:
Livio Gianfrani, Associate Professor in Experimental Physics, Dipartimento di Scienze Ambientali (DSA), Seconda Università di Napoli

ACTIVITY REPORT–2nd YEAR

RU participants:

Name-Position	Affiliation	man/month
Prof. Livio Gianfrani	DSA	6
Dr. Gianluca Gagliardi, Post-Doc fellowship	DSA	6
Dott. Antonio Castrillo, Ph.D. student	DSA	6
Prof. Dario Tedesco	DSA	2
Giovanni Casa, Technician	DSA	2

- 2nd YEAR OBJECTIVES

- Spectroscopic measurements on $^{12}CO_2$ and $^{13}CO_2$
- Joint field campaigns at Solfatara and Vulcano island
- Development of a novel diode-laser spectrometer for $^{13}C/^{12}C$ isotope ratio measurements in CO_2

- 2nd YEAR RESULTS **(max 1 page)**

During the 2nd year of the project, the Environmental Optics Group at the Environmental Sciences Department in Caserta has contributed to the optimisation of the diode-laser spectrometer for H_2O and CO_2 concentration measurements in volcanic flows, also implementing a new method for CO_2 efflux measurements. We also participated to the joint field campaigns at Solfatara volcano.

Nonetheless, most of the efforts were devoted to the development of a novel method for $^{13}CO_2/^{12}CO_2$ isotope ratio measurements, based on diode laser spectroscopy. Our goal is the demonstration that high resolution and high sensitivity laser spectroscopy can be used for accurate isotope ratio measurements in volcanic gases. We also started, on this topic, a collaboration with the Center for Isotope Research, University of Groningen (Holland).

A compact and portable spectrometer has been implemented, operating with a room-temperature DFB diode laser at the unusual wavelength of 2.007 micron, in resonance with some interesting absorption lines belonging to the CO_2 $\nu_1+2\nu_2°+\nu_3$ vibrational combination bands.

In the beginning, a spectroscopic investigation has been performed, aimed to find the optimum line pairs for isotope analysis, considering the temperature dependence of their linestrength, the possible overlapping with other atmospheric molecular species, the frequency separation as well as the ratio between the line intensities in natural abundant samples. For this purpose, the absolute intensity for a large number of CO_2 lines was accurately measured by means of a novel approach, based on the use of a Michelson interferometer in combination with pure absorption spectroscopy. As a results of the spectroscopic investigation, optimum $^{13}CO_2$ and $^{12}CO_2$ line pairs were selected.

The spectrometer is based on the use of two multiple reflection cells, the former containing the sample and the latter the standard gas. Laser absorption is simultaneously observed in the two cells using wavelength modulation spectroscopy with a 1st or a 3rd harmonic detection. Two digital lock-in amplifiers are used for phase-sensitive detection of the absorption signals.

A BASIC code was developed for system control and continuous data acquisition, while spectra analysis and retrieval of the isotope ratio were carried out through a MATLAB code. The development of the latter code has been done with a particular care, in order to satisfy a number of requirements, including the accurate determination of the $^{13}CO_2$ and $^{12}CO_2$ line centers, the

background subtraction in the detected spectra, as well as the non-linear least-squares fit of the sample-gas spectrum with the standard-gas one.
A large variety of laboratory tests have been performed to determine the precision levels in the super-ratio determination. The earlier tests were performed using pure CO_2 samples, in a low pressure regime (about 1 Torr), and 3rd harmonic detection of the absorption signals. In this case, we found a 1‰-precision (absolute statistical uncertainty corresponding to one standard deviation, over 30 repeated measurements) in both the short (over few hours) and long (over several days) terms. The situation drastically changed when using CO_2-N_2 mixtures at a total pressure of about 100 Torr. Indeed, although the absorption signals were reduced, the much wider lines we observed enabled us to improve the horizontal resolution, i.e. the number of acquired points for each line profile. Hence, we were able to improve the precision level, using a 2 % mixture, up to a level of 0.2 ‰.

- _ RESEARCH PRODUCTS
  - n° of articles published on international journals: 5
  - presentations at international meetings: 2
  - presentations at national meetings: 4
  - Computation codes : 2

PUBLICATIONS LIST

G. Gagliardi, R. Restieri, G. Casa, and L. Gianfrani: "Chemical and isotopic analysis using diode laser spectroscopy: applications to volcanic gas monitoring", Opt. & Las. Eng. 37, 131-142 (2002).

E.R.Th. Kerstel, G. Gagliardi, L. Gianfrani, H.A.J. Meijer, R. van Trigt, and R. Ramaker: "Determination of the $^{2}H/^{1}H$, $^{17}O/^{16}O$, and $^{18}O/^{16}O$ isotope ratios in water by means of tunable diode laser spectroscopy at 1.39 μm", Spectr. Acta A58, 2389-2396 (2002).

G. Gagliardi and L. Gianfrani: "Trace-gas analysis using diode lasers in the near-IR and long-path techniques", Opt. Las. Eng. 37, 509-520 (2002).

G. Gagliardi, et al.: "Sensitive detection of methane and nitrous oxide isotopomers using a continuous wave quantum cascade laser", Eur. Phys. J. D 19, 327-331 (2002).

G. Gagliardi et al.: "Generation of tunable far-infrared radiation with a quantum cascade laser", Opt. Lett. 27, 521 (2002).

A. Rocco, G. Battipaglia, A. Castrillo, G. Gagliardi, A. Peressotti, M.F. Cotrufo, and L. Gianfrani: "Assessing soil respiration by means of near-infrared diode laser spectroscopy", Env. Sci. & Tech., submitted.

A. Castrillo, G. Gagliardi, G. Casa, and L. Gianfrani: "Solving the problem of the accurate determination of absolute line intensities in molecular spectra", Phys. Rev. A, submitted.

CONFERENCE PRESENTATIONS

G. Gagliardi, E. R. Th. Kerstel, and L. Gianfrani: "Isotope analysis in atmospheric relevant molecules by means of diode laser spectroscopy", INFMeeting, Annual Meeting of the National Institute for Matter Physics", Bari, 24-28 June 2002.

A. Castrillo, G. Gagliardi and L. Gianfrani: "Interferometry and absorption spectroscopy for absolute line intensity measurements of carbon dioxide around 2 micron", INFMeeting, Annual Meeting of the National Institute for Matter Physics", Bari, 24-28 June 2002.

G. Gagliardi, A. Castrillo, and L. Gianfrani: "Absolute line intensity measurements for carbon dioxide around 2 micron using interferometry and absorption spectroscopy", 17th International Conference on High Resolution Molecular Spectroscopy, Praga, 1-5 Sept. 2002.

G. Gagliardi, F. Tamassia, S. Viciani, M. Inguscio, P. De Natale, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, A. Y. Cho, "Mid and Far-Infrared Spectroscopy using a cw Quantum Cascade Laser", 17th International Conference on High Resolution Molecular Spectroscopy, Praga, 1-5 Sept., 2002.

G. Battipaglia, A. Rocco, G. Gagliardi, A. Peressotti, L. Gianfrani, M.F. Cotrufo, "Nuove prospettive per misure di flussi di CO_2 fra suolo e atmosfera in sistemi dinamici chiusi", National Congress of the Italian Society of Ecology, Urbino, 16- 19 Sept. 2002.

A. Rocco, G. Battipaglia, G. Gagliardi, A. Peressotti, M.F. Cotrufo, and L. Gianfrani: "Studio delle emissioni naturali di CO_2 da parte di suoli mediante spettroscopia laser nel vicino infrarosso", LXXXVIII National Congress of the Italian Physics Society, Alghero, 26 Sept. - 1 Oct. 2002.

Project title:
Development of a spectroscopic integrated system for remote and continuous monitoring of volcanic gases.

RU Responsible
Name-Position: Clive Oppenheimer (Lecturer)
Affiliation: University of Cambridge

ACTIVITY REPORT–2nd YEAR

RU PARTICIPANTS

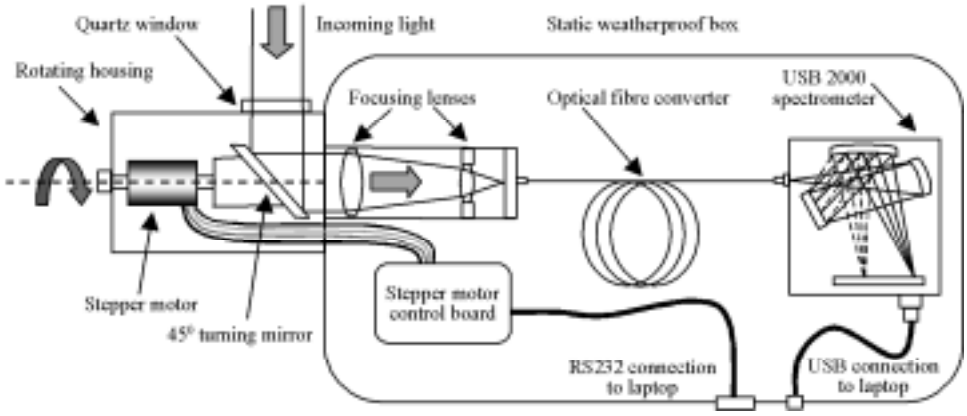
Clive Oppenheimer & Andrew McGonigle	University of Cambridge	4 months

- 2nd YEAR OBJECTIVES
- Joint field campaigns at Solfatara, Vulcano island and Mt. Etna: Testing of the spectrometers at volcanic sites.
- Upgrading and modifications of the spectrometers based on the results of the field campaigns.

- 2nd YEAR RESULTS **(max 1 page)**

We continued to develop the UV spectroscopic system that we reported in Year 1. The results continue to look very encouraging, and already there has been a considerable interest in the methodologies following our presentations at the Mt. Pelee congress and other meetings. The Montserrat Volcano Observatory now has an operational UV system based on our original work last year, and INGV-Catania has recently invested in several UV instruments for deployment on Etna.

Figure 1: Experimental configuration of the automated plume scanning device.

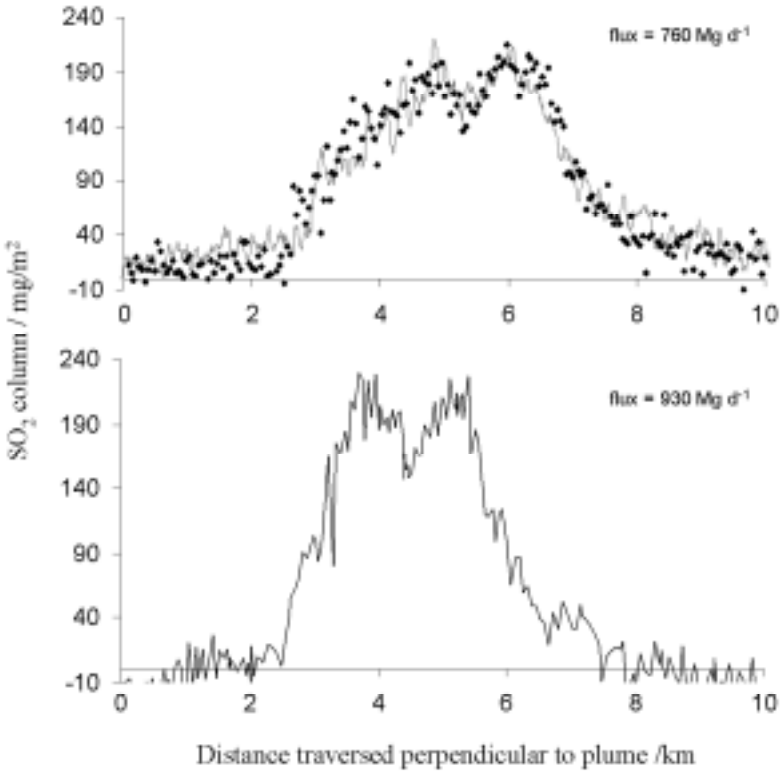


The main new achievements this year have been to design a compact, portable scanning UV system (Figure 1), and to test it in collaboration with our GNV Project colleagues from LENS and INGV during a successful field campaign in July 2002. This work has been written up and is in review with *Journal of Geophysical Research*. We measured SO_2 fluxes at Vulcano, Stromboli and Mt. Etna (averages of 14, 280 and 940 Mg d^{-1}, respectivel). Unlike the conventional approach of traversing underneath the plume, this technique can be operated from fixed positions, providing higher (every few minutes) time resolution data, and application to volcanoes where road traverses, airborne or ship

borne campaigns are impossible, impractical or uneconomic. This approach could readily be extended to measurements of other sources (e.g., industrial/agrochemical), and other UV absorbing species (e.g., NO_2). Importantly, we were able to make side-by-side measurements for Etna with a COSPEC operated by our INGV-Catania colleagues, providing an important intercomparison of the old and new methods (Figure 2).

A second field campaign at Solfatara and Vulcano is in progress now, with the UV system adapted for short path measurements using an artificial source. The aims of this work are to build a capability for optical measurement of SO_2/H_2S ratios. The results of this work will be reported next year.

Figure 2: SO_2 column amount versus distance traversed perpendicular to the plume transport direction for two traverses of Mt. Etna's plume on the 25th July 2002. COSPEC data (diamonds), obtained in parallel, are also shown in the upper plot.



- RESEARCH PRODUCTS

In press and 2002 publications on volcanic volatiles measurements are reported below. In addition, we have presented the following papers:
Keynote paper for Montagne Pelée International Congress, Martinique, May 2002 (Oppenheimer et al).
Invited paper for AGU Chapman Conference, *Volcanism and the Earth's Atmosphere*, Santorini, 2002. (Oppenheimer et al.)
Invited paper for *Workshop on Melt Inclusions*, Seiano, 2002 (Oppenheimer et al.)

PUBLICATIONS LIST (inclusive of papers in prints and accepted)

Oppenheimer, C., Pyle, D., and Barclay, J. (editors), 2003, *Volcanic degassing*, Special Publication, Geological Society of London, in press for February 2003.

Oppenheimer, C., 2003, Volcanic degassing, *Treatise on Geochemistry*, Volume 3, Chapter 6, Elsevier, in press.

Allen, A.G., Oppenheimer, C., Ferm, M., Baxter, P.J., Horrocks, L., Galle, B., McGonigle, A.J.S., and Duffell, H.J., Primary sulphate aerosol and associated emissions from Masaya volcano, Nicaragua, *Journal of Geophysical Research-Atmospheres*, in press.

Burton, M., Allard, P., Murè, F., and Oppenheimer, C., FTIR remote sensing of fractional magma degassing at Mt. Etna, Sicily, in *Volcanic degassing*, Geological Society Special Publication, in press.

Edmonds, M., Oppenheimer, C., Pyle, D.M., Herd, R., Rainwater and ash leachate analysis as a proxy for plume chemistry at Soufrière Hills Volcano, Montserrat, in *Volcanic degassing*, Geological Society Special Publication, in press.

Horrocks, L., Oppenheimer, C., Burton, M., Duffell, H., Compositional variation in tropospheric volcanic gas plumes: evidence from ground-based remote sensing, in *Volcanic degassing*, Geological Society Special Publication, in press.

McGonigle, A.J.S., & Oppenheimer, C., Optical sensing of volcanic gas and aerosol emissions, in *Volcanic degassing*, Geological Society Special Publication, in press.

McGonigle A.J.S., Oppenheimer C., Galle B., Mather T. and Pyle D., Walking traverse and scanning DOAS measurements of volcanic gas emission rates, *Geophysical Research Letters*, DOI 10.1029/2002GL015827, 26 October 2002.

Porter, J.N., Horton, K., Mouginis-Mark, P., Lienert, B., Lau, E., Sutton, A.J., Elias, T., and Oppenheimer, C., 2002, Sun photometer and lidar measurements of the plume from the Hawaii Kilauea volcano Pu‘u ‘O‘o vent: estimates of aerosol flux rates and SO_2 lifetime, *Geophysical Research Letters*, DOI 10.1029/2002GL014744, 23 August 2002.

Galle, B., Oppenheimer, C., Geyer, A., McGonigle, A., Edmonds, M., and Horrocks, L.A., 2002, A miniaturised ultraviolet spectrometer for remote sensing of SO_2 fluxes: a new tool for volcano surveillance, *Journal of Volcanology and Geothermal Research*, 119, 241-254.

Richter, D., Erdelyi, M., Curl, R.F., Tittel, F.K., Oppenheimer, C., Duffell, H.J., and Burton, M., 2002, Field measurement of volcanic gases using tunable diode laser based mid-infrared and Fourier transform infrared spectrometers, *Optics and Lasers in Engineering*, 37, 171-186.

Oppenheimer, C., Burton, M.R., Durieux, J., and Pyle, D.M., 2002, Open-path Fourier transform spectroscopy of gas emissions from a carbonatite volcano: Oldoinyo Lengai, Tanzania, *Optics and Lasers in Engineering*, 37, 203-214.

Oppenheimer, C., Edmonds, M., Francis, P., and Burton, M.R., 2002, Variation in HCl/SO_2 gas ratios observed by Fourier transform spectroscopy at Soufrière Hills Volcano, Montserrat, in Druitt, T.H., and Kokelaar, P. (eds) *The eruption of Soufrière Hills Volcano, Montserrat, from 1995 to 1999*. Geological Society, London, Memoir, 21, 621-639.

Edmonds, M., Pyle, D., and Oppenheimer, C., 2002, HCl emissions at Soufrière Hills Volcano, Montserrat, West Indies, during the second phase of dome-building: November 1999 to October 2000, *Bulletin of Volcanology*, 64, 21-30.

Project title:
Development of a spectroscopic integrated system for remote and continuous monitoring of volcanic gases.

RU Responsible
Name-Position: Frank K. Tittel (Professor of Electrical and Computer Engineering)
Affiliation: Rice University

ACTIVITY REPORT–2nd YEAR

RU PARTICIPANTS

Name-Position	Affiliation	man/month
Dr. M.Erdelyi	Rice University	2 months
Dr.D.Richter	National Center for Atmospheric Research	1 month
Dr.A.A.Kosterev	Rice University	1 month
Prof.F.K.Tittel	Rice University	1 month

- 2nd YEAR OBJECTIVES
- Upgrading and modifications of the spectrometer
- Joint field campaign at Solfatara

- 2nd YEAR RESULTS **(max 1 page)**

The thrust of our research and development project was focused on three tasks:

(1) $^{13}CO_2/^{12}CO_2$ isotopic ratio measurements using a difference frequency-based sensor operating at 4.35 microns (~2300 cm^{-1}).

A portable modular gas sensor for measuring the 13C/12C isotopic ratio in CO2 present in volcanic emissions with a precision of $1^0/_{00}$ was completed . Such an instrument can provide valuable information about CO2 exchange processes in volcanic emissions that are useful in predicting increased volcanic activity. Details of this laser based spectroscopic sensor, the required specialized absorption cell and gas sampling, the experimental strategy for measuring isotopic ratios by means of direct absorption spectroscopy and the associated data acquisition methodology are described in Publ. 1, which can be viewed on our website http://www.ece.rice.edu/lasersci . The main limitation factors of the system during laboratory test were inherent detector noise and imperfect N_2 purging of the open path part of the sensor. These error sources can be significantly reduced by increasing the difference frequency generation (DFG) power (e.g. using higher power seed laser sources or different DFG pump sources operating at ~ 1 and ~1.5 microns as described in Publ. 2). Hence, the instrumentation available in July 2002 was considered not to be ready and robust enough for field work at Solfatara with the INO/DSO and CU groups

(2) Design and implementation of a second advanced mid-IR difference DFG source based on experiences in task 1.

This source will employ the latest enabling photonics technology available in 2003. tunable DFG radiation at 4.35 microns will obtained by mixing two pump wavelengths at 1.13 and 1.52 microns from a Yb^{3+} doped DFB fiber laser and tunable DFB diode laser. Both lasers attain linewidths down to 100kHz, which is important for achieving good sensor selectivity in the presence of absorption by

interfering gas species. The power level of both pump lasers can be boosted by Yb and Er/Yb doped fiber amplifiers. Based on performance data from our previously developed DFG sources, the expected DFG power will exceed 0.1 mW if pumped with 0.2W and 0.5 W at 1.52 and 1.13 microns, respectively

(3) Design and implementation of a quantum cascade laser source for high–precision $^{13}CO_2/^{12}CO_2$ isotopic ratio measurements.

Another approach is to utilize a less complex and more compact spectroscopic source that makes use of a newly developed thermoelectrically cooled, pulsed quantum cascade laser operating in a single frequency mode at 4.35 microns. For this reason we placed an order of such a laser from Alpes Lasers in Neuchatel, Switzerland., the only commercial source to date for such lasers. To-date Alpes has not been able to fabricate and deliver such a laser that can be current and temperature tuned to two optimum $^{13}CO_2$ and $^{12}CO_2$ absorption lines at 2311 cm^{-1} in order to measure changes in ^{13}del with a precision of $0.1^0/_{00}$ This requires achieving a near equivalence in the absorption for the minor and major CO_2 isotopes, which differ in abundance by ~100. In the meantime we have designed and built a suitable laser housing, and the necessary laser current and thermoelectric temperature control electronics to operate such a pulsed DFB quantum cascade (See Publ. 3)

- RESEARCH PRODUCTS
  - **n° of articles published on international journals = 2**
  - n° of articles published on national journals, proceedings, technical reports
  - invited papers and talks
  - **presentations at international meetings = 1**
  - presentations at national meetings;
  - Data bases
  - Computation codes
  - Other

PUBLICATIONS LIST (inclusive of papers in prints and accepted)

1. M. Erdelyi, D. Richter and F.K. Tittel, "$^{13}CO_2/^{12}CO_2$ isotopic ratio measurements using a difference based sensor operating at 4.35 microns", Applied Physics **B75**, 351-357 (2002).
2. D. Richter, A. Fried, B.P. Wert, J.G. Walega, and F.K. Tittel, "Development of a tunable mid-IR difference laser source for highly sensitive airborne trace gas detection", Applied Physics **B75**, 281-288 (2002)
3. A,A Kosterev, R.F.Curl, F.K.Tittel, R.Koehler,C.Gmachl, F.Capasso, D.L.Sivco, A.Y Cho, S. Wehe and M. Allen, Room Temperature quantum cascade laser based gas sensor for continuous monitoring of atmospheric CO", Applied Optics **41**, 1169-1173 (2002)
4. M.Erdelyi,R.F.Curl and F.K.Tittel, "Portable diode laser based sensor for $^{13}CO_2/^{12}CO_2$ isotopic ratio measurements" Optical Society of America Annual Meeting, Long Beach, CA (Oct 14-18, 2001)