Please complete and return to:

NERC Field Spectroscopy Facility
Grant Institute
School of GeoSciences
University of Edinburgh
West Mains Rd
Edinburgh, EH9 3JW

For Official use only

Date received: ____________________

Application number: _______________

Alpha rating: _____________________

ARSF supported: __________________

It is a condition of loan that all applicants are expected to present the results of their research at the FSF Users meeting, and all publications arising as a direct result of your loan should fully acknowledge the support of the facility. Failure to do so may jeopardise future loans.

1. Principal Investigator (P.I.) / Applicant

Name of PI: **Dr Martin King**

Status/job title: **Lecturer**

Address: **Department of Geology, Royal Holloway University of London, Egham, Surrey**

Post code: **TW20 0EX**

Telephone:

Email:

2. User (if different from applicant)

User (if different from PI):

Status/job title:

Address:

Post code:

Telephone:

Email:

3. Equipment and measurements.

Please select the instrument(s) you wish to borrow and indicate what types of measurements you will be making. Detailed information regarding instrument specifications is available on our website at http://fsf.nerc.ac.uk

Instrument	Wavelength range	
ASD FieldSpec Pro	350 - 2500 nm	☐
GER3700	350 – 2500 nm	☐
GER1500	350 – 1100 nm	☒
GER1500 dual FOV	350 – 1100 nm	☐
Microtops	Sun photometer	☐

Types of spectroradiometer measurement

Reflectance ☐

Radiance ☒

Irradiance ☐

4. Is training required? (NB if the person U̲S̲I̲N̲G̲ the equipment has N̲O̲T̲ already been trained by FSF, then attending a training course in Edinburgh is compulsory). We provide fully customised, one-to-one training courses tailored to individuals' needs. We also offer refresher courses for those who have not used the equipment for over 18 months, or if requested.

YES ☒ NO ☐ Refresher course ☐

5. Period of Loan Dates when equipment is required (inclusive)

1st choice **ASAP – 15th Dec 2004** 2nd choice **1st Oct – 15th Dec 2004**

6. Research Project Title (maximum of 12 words)

Climatic Effects of Snow Interstitial Photochemistry (CESIP)

7. Proposed site(s) (Please provide latitude and longitude or national grid area)* **Working from Terra Nova, Italian Antarctic Base, Antarctica. 74° S, 164° W**

8. Other personnel involved in project (please provide names, affiliation and status)

N/A

9. Funding type. *Please note that loan priority will be assigned to those projects currently in receipt of a NERC Grant or studentship*

a. Project funding

NERC Research Grant ☐ (specify in section **c**)   NERC other ☐ (specify in section **c**)   Other academic ☒ (please specify below)   Other ☐ (please specify below)

Minstero dell'Istruzione dell'Universita e della Ricerce. Porgramma Nazionale di Richerche Antartide (Italian Government)

b. User/studentship funding

NERC studentship ☐ (including NERC CASE or tied studentships)   Other studentship ☐   No associated studentships ☒

c. NERC funding details. If in receipt of NERC funding please provide the full grant or studentship reference number and the title of the project

10. Science areas

a. Please indicate which ONE of the following science area is the most fitting for your application.

Atmospheric	☐	**Earth Observation**	☐
Earth	☐	**Science Based Archaeology**	☐
Marine	☐	**Polar**	☒
Terrestrial & freshwater	☐		

b. Please indicate which NERC Science Priority Area is the one most relevant to your requested loan.

Earth's life support systems – water, biogeochemical cycles and biodiversity	☐
Climate change – predicting and mitigating the impacts	☒
Sustainable economies – identifying and providing sustainable solutions to the challenges associated with energy, land use and hazard mitigation	☐
Underpinning science - used mainly when expenditure relates to the funding categories infrastructure, specialist major infrastructure or major capital projects	☐
Specific research - research on science NOT impacting on the first three priority areas	☐

11. ARSF applications

If this application is in association with an Airborne Remote Sensing Facility (ARSF) proposal, please provide the ARSF reference number, PI name, project title, requested flight dates and grade below.

ARSF Application Number: **N/A**

Principal Investigator:

*Please note that if you wish to take the equipment out of the UK during your loan you should provide further justification for your choice of site in section 9. EPFS staff will be able to advise on customs issues, and will provide essential paperwork for your trip, but export and import will be the sole responsibility of the P.I. in charge of the project.

Full Title of ARSF Project:

Requested Flight Dates: Grade:

12. Previous FSF loans

a. Is this application associated with any previous applications to FSF? If so please provide the loan reference number(s), the name(s) of the Principal Investigator(s), and the grade(s) of each.

402.0702. PI Dr Martin King

b. Please list the outputs from your previous loan(s), in terms of publications, presentations etc?

13. Research Programme: Scientific background to your proposal

Please use the space below to give details of the scientific aims and objectives of the project. Please describe in full the purpose of the study and why it is important. You should place the study in the wider scientific context, and cite related work from the published literature. Make sure you provide adequate justification for how field spectroscopy will contribute to your research. Details of how the science you intend to undertake will contribute to scientific knowledge, and how it will fit with the aims of the NERC Strategy "*Science for a Sustainable Future*" should also be included. If your research will be conducted overseas you should provide justification for taking the equipment abroad.

Science Case:

Snow forms a porous media that remains permeable to gases over several meters and is transparent to solar radiation over several decimetres (Albert et al., 2000, King and Simpson, 2002). Snowpack at high latitudes or altitudes therefore offers a large illuminated surface area which interacts with atmospheric gases (Dominé and Shepson, 2002). In the last 4 years international field campaigns in the Polar Regions have observed photochemical transformations of contaminants in snowpacks (Bottenheim et al, 2002 and Jones et al. 2000). The photolysis of the nitrate anion in the snow pack is responsible for the production of the extremely reactive OH radical:

$$NO_3^- + h\nu \rightarrow NO_2^- + O \quad (1)$$
$$\rightarrow NO_2 + O^{-\cdot} \quad (2)$$
$$O^{-\cdot} + H_2O \rightarrow OH + OH^- \quad (3)$$

The photolysis of nitrate and to some degree nitrite (NO_2^-) can process fluxes of gaseous nitrogen oxides (NO, NO_2, HONO) from the snowpack, which have been measured in the field and in the laboratory (Jones et al. 2000, Honrath et al. 1999). The reaction of OH radicals with organic species in the snowpack is thought to produce fluxes of oxidised gaseous organic chemicals from the snowpack (Dominé and Shepson, 2002). This recent discovery has caused some excitement for three reasons. First, ice cores used to predict paleoclimates assume that chemicals deposited to snowpack do not undergo chemical change, secondly the atmosphere directly above a snow pack is more oxidative due to a higher concentration of OH radicals than expected (Dominé and Shepson, 2002) and thirdly fluxes of nitrogen oxides and organic compounds out of the snowpack change the local atmospheric oxidative potential of the polar regions which are typically considered pristine.

The work is part of an international project with three international PIs and will address whether feedback mechanisms between global climate change and snow interstitial photochemistry are observable in Antarctica. For the first time gaseous reactive nitrogen fluxes from the snow pack (NO, NO_2, HONO and HNO_3) will be measured with high accuracy at Campo Icaro, Antarctica. This information, together with details of snow morphology and in-snow photolysis rates this will allow us to formulate flux relations for gas exchange between snow and the atmosphere. The determination of in-snow photolysis rates requires measurement of the UV-visible radiation both in and above the snowpack. Once the flux relations for air:snow exchange have been determined we will develop a snowpack-atmosphere model to replicate our experimental results and use the model to test how global climate change (increase UV, increase temperature) may affect chemical exchange between the snow and the atmosphere. The project has three international PIs and is funded by the Italian government. The loan of the GER1500 will secure a young British researcher place on a large field campaign to a demanding location – At least three high quality, high impact publications are expected from this work. The work combines snow physicists, atmospheric and snow chemists and radiative transfer workers, from three countries.

The objectives of the work to be undertaken by this PI are:

1) To characterise the albedo and wavelength dependent extinction depth of Antarctica snow over several transects and snow fields in Antarctica. Albedo and penetration depth are required for the model.
2) Optimise a coupled atmosphere-snow radiative-transfer model (TUV-snow) based on previous work with American collaborator (Julia Lee-Taylor, Boudler, Colardo)
3) Predict in snow photolysis rate for NO_x production and flux release to atmosphere- compare with co-PIs experimental determinations.

14. Research Programme: Proposed Methodology

Please use the space below to provide details of the project methodology. This section should include details of how data will be collected and analysed, how the spectral data will contribute to the project and whether the spectral data will be related to other parameters (and if so what other parameters).

Methodology:

The program of work will be based on a tried and tested technique developed over the winter of 2003 in the Cairngorm Mountains, Scotland. The GER1500 will serve two purposes: it will collect downwelling solar irradiance whilst in-snow irradiances are measured, and it will be used to estimate the albedo of the snowpack using measurement techniques developed to successfully measure the albedo of Scottish snow. A second smaller spectrometer (provided by the PI) with a custom made fibre-optic snow-probe will record irradiance data within the snowpack at different depths and thus allow wavelength dependent snow penetration depths to be measured. A few centimeters below the surface of the snowpack the irradiance falls exponentially with depth. The snow will be excavated and the snowpack will be interrogated (grain size, density hardness and temperature) with depth. Samples of snow will be studied for the chemical constituents (mainly NO_3^-) by one of the co-PIs. Some snow will be brought back to the UK for carbon and soot content analysis. In the previous application for the GER1500, a Delta-Eddington radiative transfer model was replaced by a 6 stream DISORT model, TUV, (Stamnes, 1998) coded by collaborators in US (Lee-Taylor 2002). The TUV model couples atmosphere and snowpack radiation fields and characterises snowpacks by the albedo, soot content and the penetration depth of the incident radiation. Thus accurate knowledge of the snow morphology is not required.

The coupling of atmospheric radiation and snow radiation fields allows the model to truly represent the photochemistry occurring in the snowpack. The modelled atmospheric downwelling irradiance will be fitted to the irradiance measured by the GER1500 (with cosine adapter) by varying cloud cover, aerosol loading and ozone column. The albedo and light penetration depth data measured by the GER1500 and the PI's own spectrometer respectively will be used to constrain the snowpack radiative properties. The model will thus be able to predict a flux of photons through a spherical surface (required for photochemistry) at different depths in the snowpack. The rate of photolysis of the nitrate ion can then be calculated by integrating, over wavelength, the product of the absorption cross-section of the nitrate ion, the quantum yield and spherical irradiance flux. By integrating over depth the transfer velocity of nitrogen oxides from the snowpack can be calculated and compared to the co-PI's chemical flux measurements.

The results of the previous loan of the GER1500 to the PI demonstrated that optical regimes of differing snow types could be envisaged, polar-cold, polar-melting and temperate. The polar snow showed the most heterogeneity and lacked characterisation. The PI has previously worked with the Co-PIs in the Arctic region in 2000. The snow there was characterised by a red absorber in the snow (soil) and shallower snow (<1m). The Antarctica campaign will provide semi-infinite snowpacks which are very clean and should test the radiative and chemical models thoroughly. The solar zenith angle of the Antarctica campaign will also reach smaller values than during the Arctic campaign, and thus test the idea of flux enhancement in the top few cm of the snowpack where direct radiation is converted to diffuse radiation by multiple scattering. All other support and funding for this campaign is being provided by the Italian military and the Italian Government. Clothing and medicals will be undertaken by the British Antarctic Survey. The PI was advised that a place was available on the campaign at very short notice (2nd July 2004) and the opportunity of a funded campaign of this nature is very unlikely to ever arise again.

I include papers from my previous Arctic work, the Italian proposal, a draft of the work undertaken in Scotland.

15. Your publication record

Please provide details of your publication record from the past five years in the space provided below. All publications are important, including conference proceedings, reports and poster papers. Those articles which are not directly related to remote sensing or field spectroscopy should also be listed. Please use the additional sheet at the back of the application form if you require more space.

Publication Record:

1. M. D.King, C. E. Canosa-Mas and R. P. Wayne "Frontier molecular orbital correlation for predicting rate constants between alkenes and the tropospheric oxidants NO3, OH and O3."*Phys. Chem. Chem. Phys.*, 1999, 1, 2231–2238.
2. M. D.King C. E. Canosa-Mas and R. P. Wayne, "A structure-activity relationship (SAR) for predicting rate constants for the reactions of NO3, OH and O3, with monoalkenes and conjugated dienes" *Phys. Chem. Chem. Phys.*, 1999, 1, 2239–2246.
3. C. E. Canosa-Mas, H. R. Hutton-Squire, M. D. King, D. J. Stewart, K. C. Thompson and R. P. Wayne "Laboratory kinetic studies of the reactions of Cl atoms with species of biogenic origin: ⊗3-carene, isoprene, methacrolein and methyl vinyl ketone." *J. Atmos. Chem.*, 1999, 34, 163–170.
4. C. E. Canosa-Mas, M. D King, D.E. Shallcross and R. P Wayne "Kinetic investigation of the reaction of between the NO3 radical and peroxymethacrlic nitric anhydride (MPAN)" *Phys. Chem. Chem. Phys.*, 1999, 1, 2411–2414.
5. C. E. Canosa-Mas, M. D. King, L. McDonnell, and R. P. Wayne "An experimental study of the gas phase reactions of the NO3 radical with pent-1-ene, hex-1-ene, and hept-1-ene" *Phys. Chem. Chem. Phys.*, 1999, 1, 2681–2685.
6. C. E. Canosa-Mas, M. D.King, P. J. Scarr, K. C. Thompson, and R. P. Wayne "An experimental study of the gas-phase reactions of the NO3 radical with 3 sesquiterpenes: Alloisolongifolene, isolongifolene and 〈-neoclovene" *Phys. Chem. Chem. Phys.*, 1999, 1, 2929–2934.
7. C. E. Canosa-Mas, S. Carr, M. D. King, D. E. Shallcross, K.C. Thompson and R.P. Wayne. "A kinetic study of the reactions of NO3 with methyl vinyl ketone, methacrolein, acrolein, and methyl methacrylate" *Phys. Chem. Chem. Phys.*, 1999, 1, 4195–4202.
8. M. D. King, E. M. Dick, and W. R. Simpson. "A new method for the atmospheric detection of the nitrate radical (NO3)". *Atmos. Environ.*, 2000, 34, 685↨688.
9. M. D.King, C. E. Canosa-Mas, and R. P. Wayne. "Gas-phase reactions between RO2 + NO, HO2 , or CH3O2: correlations between rate constants and the SOMO energy of the peroxy radical" *Atmos. Environ.* 2001, 35, 2081↨2088.
10. M. D. King and W. R. Simpson. "The extinction of UV radiation in Arctic snow at Alert, Canada (82°N)" *J. Geophys. Res. Atmos.* 2001, D12, 106, 12499–12507.
11. M. D.King, C. E. Canosa-Mas, and R. P. Wayne. "A structure-activity relationship (SAR) for predicting rate constants for the reaction of nitrogen dioxide (NO2) with alkenes" *Phys. Chem. Chem. Phys.*, 2002, 4, 295–303.
12. Carlos E. Canosa-Mas, Justin M. Duffy, Martin D. King, Katherine C. Thompson and Richard P. Wayne. "The Atmospheric Chemistry of Methyl Salicylate - Reactions with Atomic Chlorine and With Ozone" *Atmos. Environ.*, 2002, 36, 2201–2205.
13. W. R. Simpson, M. D. King, H Beine, R.E. Honrath, and X. Zhou. "Radiation-transfer modeling of snow-pack photochemical processes during ALERT 2000" *Atmos. Environ.* 2002, 36, 2663–2670.
14. W. R. Simpson, M. D. King, H. Beine, and R.E. Honrath "Atmospheric photolysis rates during the Polar Sunrise Experiment ALERT200 field campaign" *Atmos. Environ.,* 2002, 36, 2471–2480
15. H. J. Beine, F. Dominé, W.R. Simpson, R.E. Honrath, R. Sparapani, X. Zhou and M.D. King " Snow-pile and chamber experiments during the Polar Sunrise Experiments 'Alert 2000': exploration of nitrogen chemistry" *Atmos. Environ.,* 2002, 36, 2707–2719.
16. M.D. King and K.C. Thompson "Rate constants for the reaction of NO and HO2 with peroxy radicals formed from the reaction of OH, Cl or NO3 radicals with alkenes, dienes and 〈,®-unsaturated carbonyls compounds" *Atmos. Environ.*, 2003, 37, 4517-4527.
17. D.C.S. Beddows, R.J. Donovan, M.R. Heal, M.D.King, D.H. Nicholson, and K.C. Thompson "Correlations in the chemical composition of rural background atmospheric aerosol in the UK determined in real time using time-of-flight mass spectrometry" *J. Environ. Monit.*, 2004, 2, 124 - 133.

16. What output is expected from the research? (Please indicate expected output types and time scales)

1) At least four high-class international collaborative research papers of snowpack photochemistry
2) The expansion of the TUV-snow radaitive-transfer model to Antarctic snowpack. (This code is freely available to the modelling community and at present the atmospheric modelling group at Cambridge are using my previous results and this code to predict the effect of snowpack photochemistry on the global level).
3) The data gained will be analysed by a Phd student (presently 2nd year) and contribute to her thesis.

17. Declaration

I have read and agree to abide by the Conditions of Loan.

Signature of Applicant ______________________________ Date ______________

Signature of Head of Department or Institute Director ______________________________ Date ______________

18. Please use the additional space provided for adding further information you feel may support your application

Further information:

Included in this application are papers from my previous Arctic work, the Italian Proposal, a letter of support from the Italian PI and a very rough draft of the first of three papers from Scottish work that was supported by NERC EPFS.

References for sections 9a and 9b.

Albert, M. R., A. M. Grannas, et al. (2002). "Processes and properties of snow-air transfer in the high Arctic with application to interstitial ozone at Alert, Canada." Atmospheric Environment 36(15-16): 2779-2787.

Boudries, H., J. W. Bottenheim, et al. (2002). "Distribution and trends of oxygenated hydrocarbons in the high Arctic derived from measurements in the atmospheric boundary layer and interstitial snow air during the ALERT2000 field campaign." Atmospheric Environment 36(15-16): 2573-2583.

Domine, F. and P. B. Shepson (2002). "Air-snow interactions and atmospheric chemistry." Science 297(5586):1506-1510.

Jones, A. E., R. Weller, et al. (2000). "Speciation and rate of photochemical NO and NO2 production in Antarctic snow." Geophysical Research Letters 27(3): 345-348.

King, M. D. and W. R. Simpson (2001). "Extinction of UV radiation in Arctic snow at Alert, Canada (82 degrees N)." Journal of Geophysical Research-Atmospheres 106(D12): 12499-12507.

Lee-Taylor, J. and S. Madronich (2002). "Calculation of actinic fluxes with a coupled atmosphere-snow radiative transfer model." Journal of Geophysical Research-Atmospheres 107(D24): art. no.-4796.

Stamnes, K., S. C. Tsay, et al. (1988). "Numerically Stable Algorithm for Discrete-Ordinate-Method Radiative-Transfer in Multiple-Scattering and Emitting Layered Media." Applied Optics 27(12): 2502-2509.