EXTRACTION AND MEASUREMENT OF COSMOGENIC IN SITU ^{14}C FROM QUARTZ

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DECLARATION

I declare that this thesis is my own composition and that the work of which it is a record was carried out by me at the Scottish Universities Environmental Research Centre, and it has not been submitted in any previous application for a Higher Degree.

Philip Naysmith

ABSTRACT

Unlike ^{14}C that is produced in the upper atmosphere by the $^{14}N(n,p)^{14}C$ reaction, *in situ* ^{14}C is produced within minerals at the earth's surface by a number of spallation reactions including $^{17}O(n,\alpha)^{14}C$, $^{16}O(n,2pn)^{14}C$ and $^{14}N(n,p)^{14}C$ (Gosse & Phillips, 2001). A range of cosmic-ray produced radionuclides including ^{10}Be, ^{26}Al and ^{36}Cl, which are formed in surface minerals, are now used to establish ages for formerly un-dateable deposits, however, their long half-lives render them insensitive to recent events and rapidly eroding deposits. Pure quartz (SiO_2) is an ideal mineral for *in situ* ^{14}C dating due to its lack of cleavage in the mineral grains, ensuring resistance to contamination by atmospheric ^{14}C. This resistance to weathering under surface conditions, coupled with the relatively short half-life of 5730 years, provides a unique cosmogenic nuclide tool for the measurement of rapid erosion rates ($>10^{-3}$ cm yr^{-1}) and events occurring over the past 25,000 yr (Lal, 1991). Furthermore, recent advances in ^{14}C dating by AMS have provided the opportunity to measure the very small quantities of carbon that can be extracted from quartz.

The vacuum system that I have designed and built to extract carbon from quartz is based on that used at the University of Arizona (Lifton 1997), which uses resistance heating of samples to a temperature of approximately 1100ºC in the presence of lithium metaborate ($LiBO_2$) to fuse the quartz. In the presence of O_2, any carbon present is released and oxidised to CO_2, which is subsequently cryogenically trapped and graphitised for AMS measurement.

In previous work (Naysmith *et al*., 2004) it has been shown that the extraction system produced a stable blank value but when running Lifton's PP-4 standard sample, the system generated larger volumes of CO_2 but only half the number of carbon atoms compared to Lifton. In this study,

new data for CO_2 blank values, system blank values and new PP-4 data will be presented. The original vacuum system has been modified to try and reduce the volume of CO_2 produced from each combustion. Further improvements in the cleaning and handling of the quartz sleeves before they were used in the extraction process were implemented in an attempt to reduce the contamination associated with the combustion stage of the process. The CO_2 purification has been improved and results show that realistic volumes of CO_2 are being generated from quartz samples. A new-shielded quartz sample has been obtained from a depth of greater than 250 m. The results from this show it to have a very low ^{14}C atom content. A new sample of PP-4 quartz was obtained from the University of Arizona and the results (in ^{14}C atoms g^{-1} SiO$_2$) agree with values published by Lifton (Miller *et al*., 2006) for this sample. The data from both these samples are included in this study.

CHAPTER 1

INTRODUCTION

1.1. Introduction

In 2001, our ^{14}C research group at the Scottish Universities Environmental Research Centre (SUERC) was awarded a NERC small grant to design and build a vacuum system for extracting *in situ* cosmogenic ^{14}C (*in situ* ^{14}C) from quartz. *In situ* ^{14}C is important in surface exposure dating because its half-life is much shorter than the other routinely-measured cosmogenic nuclides and this allows the study of recent land surface exposures (past 25,000 years) and rapid erosion rates. The design of the extraction system was based on that at the University of Arizona (Lifton, 1997) as it was the only working system in the world at that time. Preliminary measurements and results for this new system were presented at the 18th International Radiocarbon Conference in New Zealand (Naysmith *et al.*, 2004) with the main positive conclusions being that: 1) the system we had designed, built and tested was capable of giving consistently low ^{14}C system blanks and 2) 100% recovery of CO_2, added to the system, was routinely achievable. However, on the negative side: 1) the shielded and surface quartz samples that were analysed generated larger volumes of CO_2 than Lifton *et al.* (2001) routinely measured and 2) the results from the surface quartz sample (PP-4) obtained from the University of Arizona and used by them as an in-house standard, only generated half the expected number of ^{14}C atoms. The objectives of this present study were to re-design the system and amend the methodologies to resolve the problems outlined above in order to produce numbers of ^{14}C atoms and volumes of CO_2 for system blanks, shielded quartz and surface quartz samples (PP-4) that were consistent with those determined by Lifton *et al.* (2001).

Surface exposure dating using cosmic ray-produced nuclides such as ^{10}Be, ^{26}Al, ^{36}Cl, ^{3}He and ^{21}Ne has revolutionised glacial and process geomorphology over the past decade by establishing accurate ages for formerly un-dateable deposits (Gosse and Phillips, 2001; Cerling and Graig 1994b). These nuclides are produced when cosmic-radiation-produced neutrons, and a much smaller muon component, interact with target elements in minerals at the earth's surface to produce, *in situ*, extremely small quantities of cosmogenic nuclides (Gosse and Phillips, 2001). In order to obtain an accurate surface exposure age, the geomorphic surface must be continuously exposed and erode either extremely slowly or at a known rate.

The techniques for measuring cosmogenic isotopes first started to appear in the literature in the late 1970s and early 1980s (Elmore *et al.*, 1979; Klein *et al.*, 1982; Middleton *et al.*, 1983) making significant advances from the early work of Lal and Peters (1967). One of the main problems was a lack of analytical instrumentation capable of making the measurements on very small concentrations of most cosmogenic nuclides produced at the earth's surface. It was in the early 1980s that accelerator mass spectrometry (AMS) started to make measurements on carbon and other cosmogenic isotopes possible.

In situ ^{14}C is produced by spallation reactions such as ^{16}O(n,2pn)^{14}C and ^{17}O(n,α)^{14}C (Gosse and Phillips, 2001). The main reasons for measuring *in situ* ^{14}C are: 1) it can be measured on a single quartz sample along with ^{10}Be and ^{26}Al, 2) it has a short half life (^{14}C $t_{1/2}$ = 5730 yr) compared to other cosmogenic nuclides (^{10}Be ($t_{1/2}$ = 1.5 x 10^6 yr), ^{26}Al ($t_{1/2}$ = 7.05 x 10^5 yr), or ^{36}Cl ($t_{1/2}$ = 3.01 x 10^5 yr)). In theory, both burial effects and erosion rates can be resolved by measuring multiple radionuclides with differing half-lives. In practice, however, the multiple-radionuclide approach does not give useful information for most samples deriving from the last glacial period because the long half-lives of these isotopes require burial times of

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>150 - 200 kyr for differential decay to be measurable. By virtue of its short half-life (5730 yr), however, *in situ* ^{14}C can be used together with long-lived cosmogenic nuclides to help unravel complex exposure histories involving burial or erosion during the past 25 kyr. After 25 kyr of exposure or re-exposure, *in situ* ^{14}C is present in levels that are indistinguishable from unburied surfaces.

Over the last 30 years there has been rapid development of methods for extracting stable carbon and *in situ* ^{14}C from extra-terrestrial silicates, which are now being used routinely by researchers. The development of methods for extracting *in situ* ^{14}C from terrestrial silicates has lagged behind due to the difficulty in extracting the very low concentrations that are present. The difference in *in situ* ^{14}C activity between extra-terrestrial silicates and terrestrial silicates is that the latter are about two orders of magnitude lower. In reality, developing a method that can extract the very low concentrations of *in situ* ^{14}C from terrestrial silicates has proved to be very problematic, due to the difficulties in separating it from atmospherically produced ^{14}C contamination and it was not until the 1990s when new techniques to extract ^{14}C from quartz were developed at the University of Arizona (Lifton, 1997).

Pure quartz (SiO_2) is an ideal host mineral for *in situ* ^{14}C analysis because: 1) production is dominantly by spallation of oxygen, 2) its lack of cleavage makes it highly resistant to weathering and contamination by atmospheric ^{14}C, 3) it is easily purified by etching with HF and HNO_3, 4) it is extremely common in the surface environment and 5) other cosmogenic radionuclides can also be measured in quartz. Quartz samples from several research groups are already being measured routinely for ^{10}Be, and ^{26}Al at SUERC and it would be advantageous to develop an *in situ* ^{14}C measurement capability to assist in unravelling complex dating issues.

1.2. History of Surface Exposure Dating

One of the earliest published papers on *in situ* cosmogenic isotopes was published in 1955 when Davis and Schaeffer measured the ^{36}Cl activity in a phonolite from Cripple Creek, Colorado (Davis and Schaeffer, 1955). The authors calculated an exposure age of 24000 ± 4000 yr for the Cripple Creek site - only possible because the site had surfaces that had been subject to insignificant erosion over the exposure time period. The sample contained high concentrations of Cl which were extracted from more than 4 kg of rock. The sample was counted using beta counting techniques and required 13 g of Cl to make the analysis. Lal (1958), Lal *et al.* (1958, 1960) and Lal and Peters (1967) produced syntheses of the data for nuclear disintegrations in the stratosphere and troposphere. This model for star production rates (NB. Stars are multi-pronged tracks recorded in a plastic emulsion that define the paths of particles emitted during reactions between cosmic rays and atomic nuclei) known as Lal's Global Star Production Model can be used to normalise terrestrial cosmogenic nuclide production rates on the Earth's surface.

In the twenty years from the mid-1960s to the mid-1980s it was recognized that it was possible to use cosmic-ray derived nuclides produced in rocks to date exposure times, however, this excluded rare radionuclides with long half lives where analytical extraction and measurement techniques had not been developed. The main problem was the measurement techniques for the very low concentrations of *in situ* cosmogenic nuclides found in rocks. The development of AMS in the early 1980s provided an ultra-sensitive means of counting atoms. The most commonly measured radionuclide using an AMS is ^{14}C, but now many other isotopes such as ^{10}Be, ^{26}Al, ^{36}Cl and ^{129}I are routinely measured. The first dedicated AMS systems were based on the Mark I Tandetron developed by Purser and his colleagues (Purser *et al.*, 1980) and were installed in Toronto, Oxford and Arizona. At the same time, several physics laboratories added an AMS

component to their research programs. Research groups now had the capability to measure isotopic ratios as low as 10^{-15} (Klein *et al.*, 1982; Elmore and Phillips, 1987) with a total analytical reproducibility as low as <3%. AMS now became the measurement tool for cosmogenic dating and research papers began to appear in the scientific literature covering a range of isotopes and scientific applications, such as the measurement of ^{36}Cl concentrations in lava flows (Phillips *et al.*, 1986), the determination of ^{10}Be origin in Columbia River basalt (Brown *et al.*, 1982) and the empirical determination of ^{26}Al and ^{10}Be production rates (Nishiizumi *et al.*, 1986). The development of techniques to measure *in situ* ^{14}C took until the early 1990s (Jull *et al.*, 1992; Jull *et al.*, 1994a).

With the advances in AMS measuring techniques and a greater understanding of the *in situ* production of cosmogenic nuclides that has been acquired since the early 1980s there has been a large increase in applications of cosmogenic isotope analysis in geomorphology and other related fields in quaternary science. In parallel, there has been a rapid increase in research papers from 5-6 papers in the early 1990s to 20 or more in 2002 (Cockburn and Summerfield, 2004).

1.3.   Formation of Cosmogenic Nuclides

Professor Edward Evenson, when teaching geomorphology and terrestrial cosmogenic nuclide dating, compared the degree of redness of a person's skin to the duration of exposure to sunlight. Although the comparison is not direct, it is effective because many of the same principles, factors and uncertainties that apply to the suntan clock also apply to the terrestrial cosmogenic nuclide technique. Solar radiation varies depending on elevation, latitude and time, and so does the secondary cosmic-ray flux. A tan will gradually wear away and cosmogenic radionuclides decay. Suntan lotion and hats will shield the skin from the solar radiation, while the atmosphere, snow and mountains shield the landform from cosmic radiation. Not everybody tans to the same degree of redness and

likewise, terrestrial cosmogenic nuclide production rates vary in different minerals. The change in the colour of a sunburnt epidermis after peeling may result in an overestimate or underestimate of the total sunlight exposure time. If returning for a second day of tanning, the person will begin partially tanned from the previous exposure, just as cosmogenic isotopes may be inherited from exposures prior to the present duration (Gosse and Phillips, 2001).

The principal components of a cosmic ray flux are protons, alpha particles, secondary neutrons and muons. The main difference between extra-terrestrial and terrestrial exposure studies is due to the degree of shielding - in terrestrial studies, low angle incident cosmic rays are shielded by the Earth's atmosphere whereas in an extra-terrestrial situation there is no shielding. The cosmic ray energy spectrum in the atmosphere is invariant below 12 km (atmospheric depth = 200 g cm^{-2}) (Lal and Peters, 1967).

Cosmogenic isotopes are produced by spallation reactions induced by high energy nucleons, secondary thermal neutron capture reactions, and by muon induced reactions (Lal and Peters, 1967). A spallation reaction is a nuclear reaction resulting from the collision of a highly energetic nucleon (usually a secondary cosmic-ray neutron of energy >10 MeV in the case of *in situ* terrestrial cosmogenic nuclides) with a target nucleus (Templeton, 1953). The mechanics of spallation involves two steps - the first step being the shattering of the target nucleus in the initial collision from which the primary particle may escape; the second step being disintegration of the nucleus until the energy falls below the binding energy of the individual nucleons. Galactic cosmic-ray spectra and solar cosmic-rays are made up of primary protons and alpha particles (Lal and Peters, 1967; Reedy, 1987) which strongly interact with other nuclei when they enter the Earth's atmosphere. Solar cosmic-rays are produced by the sun and have energies from 1 to 50 MeV. Most primary cosmic-rays interact with the Earth's upper atmosphere producing secondary neutrons, muons and

other secondary particles (i.e. cosmogenic isotopes such as ^{3}H, ^{3}He, ^{10}Be and ^{14}C). On Earth, the production of *in situ* cosmogenic isotopes due to solar cosmic radiation is low compared to galactic cosmic-rays. Galactic cosmic rays originate outside our solar system and have much higher energies (up to 100 GeV) than solar cosmic-rays. Galactic cosmic-rays penetrate more deeply into the atmosphere where they produce secondary particles. The secondary particles produced from the galactic cosmic-rays produce most of the *in situ* cosmogenic isotopes found in terrestrial rocks. Nucleons produced primarily from solar and galactic cosmic-rays provide ample energy for spallation reactions. Some of the important spallation reaction products for *in situ* geomorphic studies include ^{3}He, ^{10}Be, ^{14}C, ^{21}Ne, ^{26}Al and ^{36}Cl. Some spallation reactions which take place in silicate rocks are oxygen dependant producing the isotopes ^{3}He, ^{10}Be and ^{14}C.

Unlike ^{14}C that is produced in the upper atmosphere solely by the ^{14}N(n,p)^{14}C reaction, *in situ* ^{14}C is produced within minerals at the earth's surface by a number of spallation reactions including ^{17}O(n,α)^{14}C, ^{16}O(n,2pn)^{14}C and ^{14}N(n,p)^{14}C (Gosse and Phillips, 2001).

1.4. Advantages of *In Situ* ^{14}C for Surface Exposure Dating

To obtain an accurate surface exposure age, the geomorphic surface must remain exposed and erode either extremely slowly or at a known rate. One of the main advantages of using *in situ* ^{14}C for surface exposure dating is its short half-life relative to other isotopes (see Table 1).

Isotope	Half life ($t_{1/2}$)
^{10}Be	1.5×10^6 yr, (1.36×10^6 yr)*
^{26}Al	7.05×10^5 yr
^{36}Cl	3.01×10^5 yr
^{14}C	5730 yr

Table 1: Half-lives of cosmogenic isotopes

 * Nishiizumi *et al.* (2007)

In theory, both burial and erosion rates can be resolved by measuring multiple radionuclides with different half-lives and it is best to measure one with a short half life such as ^{14}C, and one with a longer half life, such as ^{10}Be. Assuming that the erosion rate is constant, the shorter half-life nuclide, ^{14}C, can be used to estimate the erosion rate of the surface as it reaches secular equilibrium in about 25 kyr. The radionuclide with the longer half-life can then be measured to determine the exposure age of the surface by compensating for any effects of erosion. The first people to suggest the two nuclide approach to surface exposure measurements were Lal and Arnold (1985) when they attempted to measure ^{26}Al and ^{10}Be from a single quartz sample. ^{26}Al and ^{10}Be exhibit different geochemical behaviours, have different half-lives and can both be extracted from quartz. In practice, however, the multiple-radionuclide approach does not give useful information for most samples deriving from the last glacial period because the long half-lives of these isotopes require burial times of >150-200 kyr for differential decay to be measurable. By virtue of its short half-life, *in situ* cosmogenic ^{14}C can be used together with long-lived cosmogenic nuclides to help unravel complex exposure histories involving burial or erosion during the last 25 kyr. *In situ* ^{14}C has a production rate about three times that of ^{10}Be in quartz, which makes quartz the ideal mineral for analysis.

One of the major advantages of using *in situ* [14]C is the opportunity to empirically estimate production rates as a function of latitude and altitude (Brook *et al.*, 1995). Over the last 20,000 years, assuming negligible erosion rates, the short half-life of ^{14}C allows attainment of secular equilibrium (*ie* nuclide production = loss from decay). To estimate the average production rate of *in situ* [14]C, scientists can now measure the number of ^{14}C atoms on a given surface at secular equilibrium. Lifton *et al.*, 2001 have demonstrated this using quartzite samples from Provo and Bonneville shorelines where primary wave rounding and polishing, still present in these samples demonstrates negligible erosion since their formation.

1.5. Previous Studies of *In Situ* [14]C

During the last 30 years there have been major steps taken to develop analytical methods for extracting *in situ* [14]C from terrestrial silicates. There are many reliable techniques for extracting stable carbon from terrestrial and extra-terrestrial silicates (Craig, 1953; Suess and Wanke, 1962; Fireman *et al*, 1976) however, the main difficulties in extracting *in situ* [14]C are the result of the lower concentrations present and also the presence of atmospherically produced [14]C. Early extraction techniques tended to involve 1-10 g of cleaned quartz being combusted at temperatures of 400-600°C to remove the surface contaminants, followed by a second combustion step with a resistance furnace (Des Marais and Moore 1984; Mattey *et al.*, 1989) or pyrolysis under vacuum with a resistance furnace before total fusion with an RF furnace (Brown *et al.*, 1984; Fireman, 1978). Jull and his colleagues (Jull *et al*, 1989a: Jull *et al.*, 1989b) started with 0.5-2 g of rock mixed with 2-4 g of iron accelerator chips as a combustion flux. This mixture was placed in a muffle furnace at 500°C for 1 hr to remove the surface contaminants and then placed in a RF furnace and heated to fusion in oxygen for 8 min. The system was flushed every 1-2 min with oxygen and the gas mixture passed through a MnO_2 trap and a CuO/Pt furnace. On completion, the excess oxygen was pumped away

and the gas passed over a water trap to collect any water vapour. The CO_2 was measured to estimate how much carbon was generated before being converted to graphite for measurement by AMS (Jull et al., 1989a; Jull et al., 1992). Most extraction techniques convert the carbon species in the sample to CO_2 prior to measurement. In the early 1990s, the research group in Arizona published a slightly different method for extracting in situ ^{14}C from rocks at high latitude (Jull et al., 1994). The revised method used 10-60 g of rock, crushed to about 1 cm size, which was chemically cleaned using HCl and HNO_3 to remove the carbonates, organics and oxides of iron and manganese prior to treatment with sodium hexametaphosphate to disperse the clays. The samples were then dried and crushed to <1 mm and between 10-60 g of total rock placed in a Mo crucible in a quartz tube surrounded by an RF coil at 500°C. A re-circulating pump then passed a mixture of helium and oxygen over the sample and the gases collected. Once the CO_2 was isolated from the water it was measured, however, this low temperature gas, generated from the contaminants, was not used in the calculation of cosmogenic [14]C. The sample was then heated to 1500°C with a new charge of helium and oxygen and the gases collected and measured. This is the gas sample used to calculate the cosmogenic ^{14}C activity of the sample. The main problems associated with this method are the substantial variation measured in the system blanks and the variable ^{14}C yield from the Mo crucibles.

Various research groups have tried different techniques to extract and isolate in situ ^{14}C from terrestrial materials; this has included generating CO and CO_2 from a single sample and then analysing them separately for ^{14}C by AMS. Research by Rowland and Libby (1953) and Pandow et al. (1960) showed that recently formed ^{14}C atoms from irradiated samples react with oxygen and form [14]CO in ratios ranging from 0.5 to 1.0 [14]CO:([14]CO + [14]CO_2). It took until the 1990s to prove this effect in polar ice (Jull et al., 1994a) and meteorites (Lal and Jull, 1994). More recent

advances include developing a method based on total dissolution of terrestrial silicates using HF (Lal and Jull, 1994). They discovered that the ratio of ^{14}CO to total ^{14}C can vary up to 25% or more among different samples. Thus, either 1) both components need to be considered for accurate *in situ* ^{14}C concentration estimates (Cresswell *et al.*, 1994) or 2) one must assume a ratio of ^{14}CO to total ^{14}C to convert ^{14}CO concentrations to total ^{14}C concentrations in the sample (Lal and Jull, 1994). During wet oxidation the blanks for both ^{14}CO and $^{14}CO_2$ were calculated from the total amount of quartz sample analysed. Two different weights of quartz were used in an attempt to lower the blank value for the system (Lal and Jull, 1994). Blank values of $0.2 \pm 0.3 \times 10^5$ atoms ^{14}C g^{-1} quartz for CO and $1.3 \pm 0.5 \times 10^5$ atoms ^{14}C g^{-1} quartz for $^{14}CO_2$ from 40-45 g of quartz have been quoted (Lal and Jull, 1994).

The next major step in the development of a reliable extraction technique for *in situ* ^{14}C was the redesigning of the systems in an attempt to improve reproducibility of system blanks from whole rock extractions (Lifton *et al.*, 2001). This system was designed to: 1) minimise the analytical variability in ^{14}C concentrations determined in samples and blanks, analysed on quartz separates, 2) be able to isolate atmospheric ^{14}C and 3) produce a low constant system blank for the whole extraction procedure. In order to achieve this, the system included a stepped combustion set-up using a re-circulating pump to circulate high purity oxygen over the sample, based on systems by Des Marais (Des Marais and Moore, 1984). Figure 1 depicts the new extraction system (Lifton, 1997), which allows the extraction technique to be viewed as three separate parts. The first part is the furnace section, which is made up of a Mullite tube inserted into a resistance furnace capable of reaching 1200°C. The sample boat, made of alumina, is placed into a quartz sleeve, which is used to protect the Mullite furnace from attack from mobile lithium metaborate. Lithium metaborate is added as flux, in the ratio of 4:1 lithium metaborate:quartz, to lower the melting point of pure quartz (1610°C to 1730°C) to below

1200°C (Deer *et al.,* 1966; Lide, 1994). There is a two stage stepped combustion process to extract the CO_2 from quartz; firstly, the tube is heated to 500°C to evolve and subsequently eliminate carbon from atmospheric contamination and then the tube is heated to 1200°C and the CO_2 produced is collected. The second part of the system is designed to purify the CO_2 using a series of traps to eliminate SO_2 and oxides of nitrogen. Once the cleanup has removed the impurities from the CO_2, the third part of the system converts the CO_2 into graphite. The results gained using this technique proved that *in situ* ^{14}C from a 5 g quartz sample exposed for approximately 500 to 600 years at sea level and high latitude can be detected (Lifton *et al.*, 2001). This extraction method produces an average blank value of $2.3 \pm 0.1 \times 10^5$ atoms ^{14}C g^{-1} quartz (Lifton *et al.,* 2001). Lifton also proved that at temperatures up to 500°C the atmospheric ^{14}C component will be removed while at temperatures above 500°C the *in situ* ^{14}C will start to be released (Lifton *et al.*, 2001).
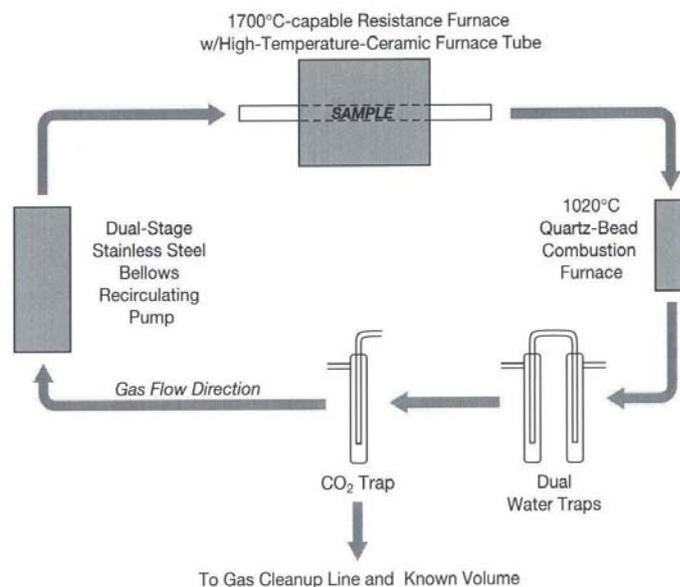
Figure 1: Schematic diagram of ^{14}C extraction system (Lifton, 1997)

For the extraction of *in situ* [14]C from carbonates, cryogenic methods are used to separate *in situ* cosmogenic [14]CO from *in situ* [14]CO_2 and any biological ^{14}C present as organic matter in the $CaCO_3$ (Handwerger *et al.*, 1999). This method uses 10 g of carbonate rock reacted with 100% H_3PO_4 prior to the addition of a dead [14]CO carrier. In the main manifold, CO_2 can be cryogenically separated (using liquid nitrogen) from CO using 250 ml removable flasks filled with lengths of glass tubing to increase the surface area. After this cryogenic separation of CO_2 from the dead CO carrier and the cosmogenic [14]CO_2, the CO is then transferred through a liquid nitrogen trap to a molecular sieve. In this, the oxidation portion of the line, the purity of the CO_2 and CO separation can be checked using a gas chromatograph. After this transfer, CO is oxidised to CO_2 using a CuO furnace at 550°C. This CO_2 is then transferred to a sample tube for quantification using a capacitance manometer and then prepared for measurement by AMS. The system blank for this system averaged 0.0105±0.0017 fraction modern carbon (FMC) after six measurements.

In 2004, Yokoyama and colleagues (Yokoyama *et al.,* 2004) published a paper on their system for extracting *in situ* [14]C from quartz using a spiked carrier gas consisting of O_2-CO-CO_2-He. Their system is based on Lifton's (Lifton, 1997) although the Yokoyama system does not use fluxing agents. They use 1 - 6 g of cleaned quartz loaded into a pre-cleaned alumina boat, placed in the furnace and heated to 450°C overnight to remove meteoric contamination. The *in situ* [14]C is then captured by heating the sample to 1550°C and passing the resultant gases over Pt chips at 500°C to convert all CO to CO_2. Using the carrier gas of O_2-CO-CO_2-He helped eliminate the contaminating oxides of nitrogen. The procedural blank for this system is typically 2.3 ± 0.2 x 10^{6} [14]C atoms per analysis, independent of the mass of the heated quartz.

In early 2000, an *in situ* [14]C extraction system was built and tested at the Scottish Universities Environmental Research Centre (Naysmith *et al.*,

2004). This system was similar to that used by Lifton at the University of Arizona (Lifton, 1997). Initial commissioning involved running a number of test samples through the system. The first test was simply to take 1 ml aliquots of the CO_2 carrier gas generated from "infinite age" Icelandic doublespar, graphitise these and measure the ^{14}C activity.   This doublespar sample, which produces "dead" CO_2, was to be used to bulk up any sample CO_2 to 1 ml for graphitization.   The results of the ^{14}C activity measured in the doublespar are shown in Table 2.

Lab. Code	Sample No. Processed	Measured Fraction Modern (Fm)*	[14]C atoms ± 1 σ (x 10^5)*
AA-51187	6	0.0050 ± 0.0012	1.537 ± 0.369
AA-51188	7	0.0033 ± 0.0011	0.811 ± 0.270
SUERC-14	27	0.0025 ± 0.0003	0.778 ± 0.093
SUERC-15	28	0.0024 ± 0.0003	0.692 ± 0.087

Table 2: [14]C activity in "dead" CO_2 dilution gas

(*Not corrected for machine background or contamination)

The next step required characterisation of the system blank for the whole process - defined here as 1 ml of doublespar CO_2 carrier gas cycled through the entire extraction and purification procedure, including all sample heating steps and in the presence of the lithium metaborate fluxing agent and ultra high purity O_2. The results indicated that 100% recovery of the gas was achieved on each occasion, however, when an F value (F_m corrected for machine background and contamination) was determined, the number of ^{14}C atoms in the system blank decreased systematically over the first seven processings of this carrier CO_2 through the full procedure (Table 3). Samples 31, 33 and 34 were more stable and close to the bulk doublespar gas in activity, suggesting that the continuous running of the vacuum system with ultra-high-purity O_2 was slowly

cleaning contaminant carbon from the line. It also demonstrated that great care must be taken to keep the line isolated from potential sources of contaminant carbon. These samples were measured at our AMS facility which opened in 2002. Since then there have been many technological developments to the AMS system which could account for some of the improvement in the doublespar background standards.

Lab. Code	Sample No.	Recovery Yield (%)	Measured F value	^{14}C atoms $\pm$ 1σ (x 10^5)
AA-52891	11	103.3	0.0524 ± 0.0012	16.007 ± 0.367
AA-52892	12	101.5	0.0237 ± 0.0011	7.374 ± 0.342
SUERC-5	20	105.0	0.0354 ± 0.0020	10.970 ± 0.620
SUERC-6	21	98.0	0.0122 ± 0.0012	3.678 ± 0.362
SUERC-7	22	102.5	0.0109 ± 0.0015	3.412 ± 0.470
SUERC-16	29	100.0	0.0070 ± 0.0006	2.061 ± 0.147
SUERC-18	31	98.7	0.0009 ± 0.0004	0.268 ± 0.089
SUERC-719	33	99.8	0.0015 ± 0.0004	0.430 ± 0.115
SUERC-728	34	101.2	0.0014 ± 0.0004	0.406 ± 0.116

Table 3: Recovery yields and ^{14}C atom content of "dead" CO_2

The results for ^{14}C extracted from 5g of quartz which had >5 m of shielding by rock with a density of ~2.7 g cm^{-3} are given in Table 4. This material should, in principle, be free from ^{14}C generated by cosmogenic neutron spallation reactions and was used in a first attempt at assessing the full system contamination based on a total quartz procedural blank for the extraction procedure. Initial analyses of the shielded quartz were found to be dominated by the high system blank (see Table 3). However, successive measurements of repeats of full chemistry blanks (using this quartz powder) did not result in a decrease to the activities measured in the doublespar dilution gas or the doublespar procedural blanks. This

would seem to indicate that this quartz contained a measurable ^{14}C concentration well above our lowest system blank level (by a factor of 10).

Lab. Code	Sample No.	Measured F value	^{14}C atomsg^{-1} SiO$_2$ ± 1σ (x 10^5)
AA-52893	15	0.0215 ± 0.0011	6.514 ± 0.333
AA-52894	16	0.0371 ± 0.0011	11.311 ± 0.335
AA-52895	17	0.0217 ± 0.0015	6.657 ± 0.460
SUERC-8	25	0.0259 ± 0.0013	7.969 ± 0.400
SUERC-9	26	0.0033 ± 0.0012	0.999 ± 0.363
SUERC-729	39	0.0232 ± 0.0006	6.681 ± 0.166

Table 4: No of ^{14}C atoms g^{-1}SiO$_2$ extracted from 5 g shielded quartz samples

Further assessment of the efficiency of the system was undertaken by analysis of a Lake Bonneville shoreline surface quartz sample (PP-4), which has been used as an internal standard at the University of Arizona (Lifton *et al.*, 2001). The geomorphic features associated with Lake Bonneville have been used to estimate late Quaternary cosmogenic production rates for ^{3}He (Cerling and Graig, 1994b), ^{10}Be (Gosse and Klein, 1996) and ^{14}C in carbonates (Handwerger, 1999). Lake Bonneville cut shorelines deeply into bedrock during several lake stillstands (Oviatt *et al.*, 1992). The chronology of the late Pleistocene lake cycle is constrained by 83 radiocarbon ages and is considered one of the most reliable in the world (see Figure 2) (Oviatt *et al.*, 1992). This lake cycle began at approximately 30 ^{14}C kyr, with levels rising until 22 ^{14}C kyr, when one or more oscillations produced the Stansbury shoreline. After about 20 ^{14}C kyr, indirect evidence from deep water sediment cores and shore-zone deposits suggests 3 lake-level fluctuations of approximately 30 to 50 m each may have occurred as the lake filled to its highest level – the Bonneville level (Oviatt, 1997). The Lake Bonneville shoreline surface

quartz sample (termed PP-4) was collected an outcrop that was resistant to erosion based on the fact that primary wav rounding and polishing were still present in the sample. This sample has been analysed many times on the system at the University of Arizona (Lifton *et al.*, 2001), resulting in it being a very suitable standard to be used to check the performance of our system.
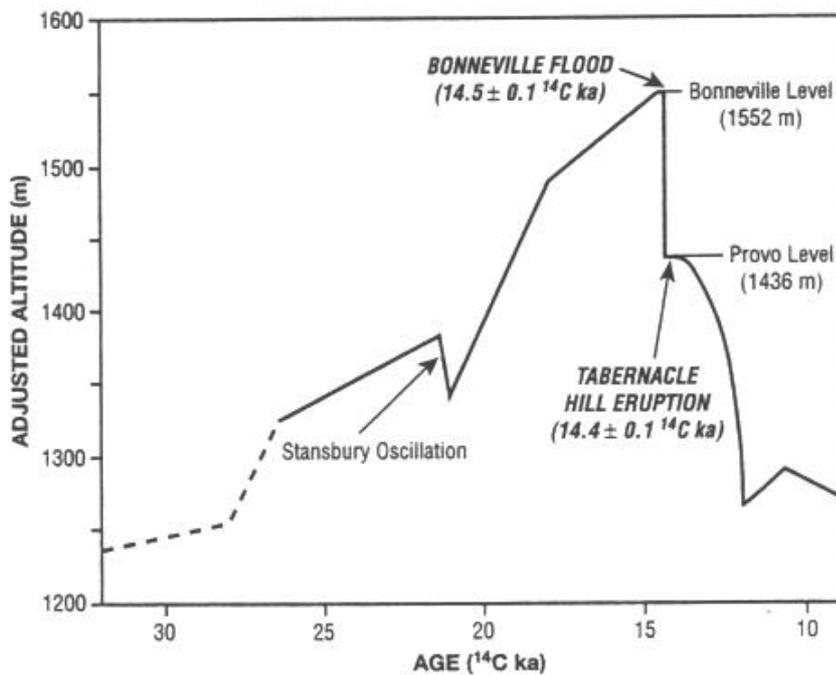
Figure 2: Generalized time altitude diagram of Lake Bonneville, Utah

The weighted mean of the analyses carried out at the University of Arizona is $3.354 \pm 0.043 \times 10^5$ atoms g^{-1} (n=14) (Lifton, *pers. comm.*). The results presented here (Table 5) indicate less than half of this number of atoms has been extracted.

Lab. Code	Sample No.	Measured F value	^{14}C atoms g^{-1} ± 1σ (x 10^5)*
SUERC-730	40	0.0258 ± 0.0006	1.386 ± 0.040
SUERC-731	41	0.0142 ± 0.0005	0.737 ± 0.035
SUERC-732	42	0.0278 ± 0.0006	1.509 ± 0.043

Table 5: ^{14}C atoms extracted per gram of PP-4 quartz

(*Net of machine background, contamination and system blank contributions as the system blank appeared stable by the time these measurements were made)

Thus, some progress had been achieved in developing a method for the extraction and measurement of in situ ^{14}C at SUERC with consistently low system blanks and 100% CO_2 recovery being achieved. However, some issues with reproducibility, removal of contaminant ^{14}C in the initial period of the study and extraction efficiencies of in situ ^{14}C (perhaps as a function of temperature) remained. The shielded quartz samples appeared to have some ^{14}C activity, possibly due to muon production. At that time, it was intended that future work would use quartz from >50 m depth and we would attempt to explain the lack of agreement between our results and those of the University of Arizona. There are a number of possibilities for this including: 1) the incomplete release of ^{14}C atoms from the sample, 2) loss of ^{14}C atoms although this seems unlikely since recovery yields are all close to 100%, 3) release of in situ ^{14}C atoms from the 500ºC combustion stage of the extraction process, resulting in a lower yield when the atoms released at 1100ºC are collected and measured and 4) differences in the extraction techniques.

1.6. Production Rates for In situ ^{14}C

Production rate, by definition is the rate at which a specific nuclide is produced from a specific element or in a mineral. Production rates may

include separate terms for spallation, muonic and thermal neutron capture interactions. Rates for all terrestrial cosmogenic nuclides vary both spatially and temporally (Cerling and Graig, 1994a; Masarik and Reedy, 1995) and are often reported as normalised to sea level and high latitude (Gosse and Phillips, 2001). They can be determined by numerical simulation of the nuclear interactions and other physical processes that would be responsible for the product nuclide (Masarik and Reedy, 1995). Most of the production rates measured have used a scaling model produced either by Lal (1991) or Dunai (2000) to calculate values for specific regions of the world. One of the earliest calculated production rates for ^{14}C was 19.8 ± 1.5 atoms $g^{-1}y^{-1}$ taken from work by Jull *et al.* (1994a) on samples from Tabernacle Hill, Utah. This value agreed well with some earlier work on whole rocks that were assumed to have reached saturation (Donahue *et al.*, 1990b; Jull *et al.*, 1992).

Table 6 below shows *in situ* ^{14}C production rates from the literature that have been calculated using Lal's model (Lal, 1991).

Reference	*In situ* ^{14}C production rate (atoms g^{-1} SiO_2 y^{-1})
Lifton *et al.* (2001)	15.1 ± 0.5
Lifton (1997)	17.0 ± 1.0
Handwerger *et al.*(1999)	17.8 ± 0.7
Jull *et al.* (1994a,b)	19.8 ± 1.5
Donahue *et al.* (1990a,b)	22.6 ± 1.7
Nishiizumi *et al.* (1989)	15.7 ± 2.6
Stone (2000)	16.3 ± 2.5

Table 6: Calculated *in situ* ^{14}C production rates

1.7. Measurement Techniques

It was not until the development of AMS in the late 1970s (Nelson *et al.,* 1977; Bennett *et al.*, 1977) that the measurement of the very small quantities of cosmogenic isotopes could be realized as a routine technique. In the late 1970s the research groups in McMaster and Rochester developed a new generation of accelerators, Tandetrons, which could measure ^{14}C in natural materials. While these early instruments were set up to routinely measure ^{14}C, other nuclear physics research facilities started to measure other isotopes (Elmore *et al.,* 1980; Klein *et al.,* 1982; Nishiizumi *et al.,* 1986). As more AMS instruments came on line, the quantity and scope of the research increased dramatically in the early 1990s (Cockburn and Summerfield, 2004). One of the most important features of AMS is the combination of the high efficiency of mass spectrometry technology, which can also discriminate against isobaric and molecular interferences, together with the ability to measure isotopic ratios for specific elements to a level of 1 in 10^{15}. There are now two types of accelerators employed in research institutes around the world. They are 1) Tandem accelerators which include pelletrons and tandetrons and 2) the new single stage accelerators (SSAMS). The new single stage AMS system designed by Suter *et al.*, (1999) (and built commercially by NEC) is based on an open air 300 kV deck and recent results show that the single stage AMS approaches the precisions available from the compact carbon AMS system without the complexity of an SF_6 filled insulating pressure vessel common to all tandem accelerators (Schroeder *et al.,* 2004).

Tandem accelerators are widely available due to older nuclear physics systems being refurbished and now being used for routine AMS measurements. Modern tandem accelerators come with a very high level of control that can achieve a level of precision for radiocarbon dating that was not possible in some of the older systems. Tandem accelerators with

terminal voltages from 500 kV to 3 MV can be used to measure isotopes with a wide range of masses such as ^{3}H, ^{7}Be, ^{10}Be, ^{14}C, ^{26}Al, ^{129}I and ^{236}U where isobaric discrimination is not a significant problem. Figure 3 shows the basic schematic for a NEC tandem pelletron accelerator, including all of the main stages from the ion source to the collection system.

Fifield (1999) gives an excellent description of the principles of operation of a tandem AMS system. These are summarised as follows: Negative ions are generated in the ion source (1) by sputtering the sample with caesium ions (the beam currents generated may vary depending on the isotope of interest. Table 7 shows typical beam currents used for a range of commonly measured isotopes). The negative ions are then pre-accelerated to 30-200 keV, and mass analysed by a magnet (2) (injector magnet). In the case of ^{14}C, ^{26}Al and ^{129}I, isobaric interferences are eliminated because ^{14}N, ^{26}Mg and ^{129}Xe do not form stable negative ions. These negative ions are then accelerated to the positive high voltage terminal of the accelerator passing through a thin carbon foil or a low pressure gas (*eg.* argon). The purpose of these is to strip off electrons to convert the negative ions to multiple-charged positive ions and cause negative molecular ions to dissociate into their component atoms which also emerge positively charged. In the second stage of the tandem accelerator (3), the positively charged ions are accelerated back to ground potential, they pass through another magnet (4) (analyzer magnet) which will select the ions of interest using a combination of charge state and energy and send them to the detector. A fraction of the molecular fragments can also reach the detector as the result of charge changing collisions with gas molecules during the second stage of acceleration. Most AMS systems therefore incorporate either a velocity filter or an electrostatic analyzer to remove such fragments. The AMS determines the ratio of the rare isotope to an abundant isotope of the same element; ^{14}C/^{12}C for example.

(2) 90 Magnet Injection System

(1) Ion Source

(3) Tandem Pelletron

ACPC

(7) Gas filled detector

(5) Faraday Cups

(6) ECA

(4) 90 C Mass energy
analysis magnet.
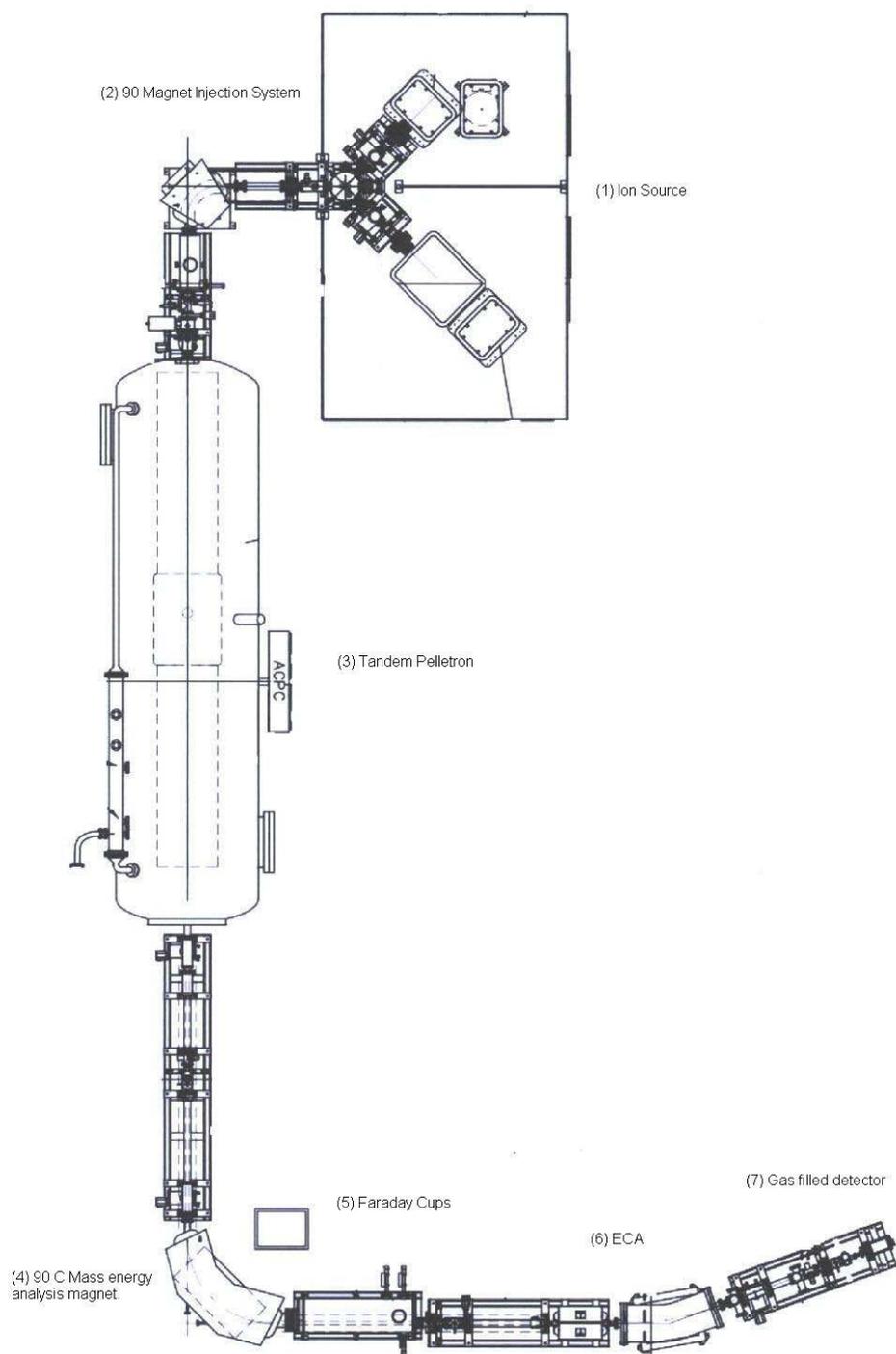
Figure 3: SUERC 5MV NEC tandem pelletron accelerator

This is accomplished by accelerating ions of the abundant isotope or isotopes as well as the rare isotope. Whereas the latter are counted individually, the former (which are typically 10^{12} times more intense) must be measured as an electrical current in a Faraday cup.

AMS Isotope	Ion injected	Ion Detected	Negative-ion currents (uA)	Precision (%)
^{10}Be	BeO^{-}	Be^{3+}	1-10	1-3
^{14}C	C^{-}	C^{4+}	15-80	1-3
^{26}Al	Al^{-}	Al^{3+}	0.1-1	1
^{36}Cl	Cl^{-}	Cl^{5+}	5-25	3
^{129}I	I^{-}	I^{3+}	2-10	1

Table 7: Typical beam currents used at SUERC 5MV AMS Facility (Maden *et al*., 2007)

The offset Faraday cup assembly (5) measures the abundant isotopes, ^{12}C and ^{13}C, which are deflected more than the heavier, rare ^{14}C isotope. The same principle holds for beryllium, aluminium, iodine, chlorine and other species. The rare isotopes are transported through a 20° electric cylindrical analyzer (ECA) (6) to filter out any other possible interfering ions for an overall system sensitivity of better than 1 in 10^{15}. Interfering background levels are reduced to a few parts in 10^{16}. The rare isotope ions which were selected through the analyzing magnet and ECA are counted in a gas ionisation detector (7). The gas is ionized by the collision with the high energy ions, and it is possible to analyse the target isotope ions separately by collecting and quantifying the electric charges. In this way, ratios of $^{14}C/^{12}C$ and $^{14}C/^{13}C$ are measured with precisions of better than 0.3% routinely obtained.

1.8. Applications using *in situ* [14]C

There are many types of applications in the literature relating to cosmogenic nuclide dating (Cockburn and Summerfield, 2004; Tuniz *et al.,* 1994; Gosse and Phillips, 2001). The wide range of applications in geomorphology can be split into two distinct groups: 1) dating geomorphological events and 2) measuring incremental changes in the earth's landscape. A geomorphological event in this context is a change in the landscape that, in relation to the background rate of modification, represents an immediate occurrence of sufficient magnitude to expose an area that had been effectively shielded from cosmic radiation *eg.* a landslide down a mountain to expose fresh rock. An incremental change to the earth's landscape is when there are small changes due to progressive weathering that slowly strip away small quantities of material from the surface. When considering incremental change it is important to consider the net effect of cosmogenic nuclide production and the prevailing rate of erosion when considering the apparent age of the landscape.

Using *in situ* [14]C to determine ages for surfaces from previously undated landscapes is now well documented. Lake Bonneville in Utah and Southern Idaho has well dated bedrock surfaces (Oviatt *et al.*, 1992) and was selected by Lifton to test his extraction procedures for *in situ* [14]C. Lifton collected quartz samples from Bonneville and Provo shorelines and although the results he obtained differ at 2σ from Lake Bonneville shoreline carbonates by Handwerger *et al*. (1999) this was explained as discrepancies due to the reduction of contaminant ^{14}C and other sources of variability in his improved techniques (Lifton *et al.*, 2001). *In situ* [14]C and [36]Cl have been used to try and understand the complex exposure history of Arctic Landforms (Zreda and Lifton, 2000). Both nuclides will accumulate during periods of exposure. The long lived [36]Cl remains approximately constant during short periods of burial; thus, its

concentration reflects the cumulative exposure. The short lived ^{14}C decays during periods of burial; its concentration reflects the length of exposure and burial. The critical information is the difference between the measured concentrations of the two nuclides. If the two nuclides give the same age then it is a case of continuous exposure but if the ^{14}C is depleted because of decay then it is a case of burial. The analysed boulder samples and the data indicated two deglaciation events, one at 10 ky and the other at 74 kyr. Both results were consistent with other deglacial data from this region. The results indicate that the combination of ^{14}C and a longer lived nuclide (^{36}Cl, ^{26}Al, ^{10}Be, ^{3}He, ^{21}Ne) can be used to unravel complex exposure histories of late Quaternary glacial surfaces.

Nishiizumi et al., (1993) measured sand dune samples using ^{10}Be and ^{26}Al and produced exposure ages of 70-100 x 10^3 yr. In contrast Lal and Jull (1994) measured ^{14}C exposure ages of 1-10 x 10^3 yr indicating that the sands measured were not exposed continually on the surface. The sands were probably shielded for an appreciable time by an overlying sand mass in the past.

While this is a large step forward there are certain places on earth where quartz minerals cannot be found, usually in basaltic terrains. Pigati et al. (2007) have developed a chemical procedure to clean up olivine and have built a vacuum system which has a low extraction blank capable of making routine in situ ^{14}C measurements on olivine. This procedure is based on a variation of Lifton's method and was developed because olivine did not withstand the aggressive pre-treatment method that is used on quartz but reacted better when using HNO_3. The incomplete recovery of the in situ ^{14}C component during this extraction method was corrected for in the use of a factor based on the Fe:total carbon ratio of the sample. The data, after this correction, matched the expected values from the literature for Tabernacle Hill and McCarty's flow samples (Pigati et al., 2008)

Most of the applications using *in situ* ^{14}C have concentrated on calculating the production rate of ^{14}C in quartz as a function of altitude and latitude as discussed above and illustrated in Table 6.

A further application uses *in situ* ^{14}C produced in a quartz vein from Macraes Flat, East Otago, New Zealand, to confirm concentrations of *in situ* produced ^{10}Be and ^{26}Al previously measured at this site (Kim and Englert, 2004). In this study, results are presented for cosmogenic ^{14}C in quartz sampled up to depths of 400 g cm^{-2} (1.45 m) from a mine at Macraes Flat (Kim *et al*., 2007). The measurements were carried out with two goals: 1) to check on the production rates of ^{14}C in Si and O by the secondary particles of cosmic radiation (neutrons and muons), and 2) to see if ^{14}C concentrations can put any constraints on the erosion rates beyond what was learnt from the ^{10}Be and ^{26}Al measurements from quartz from the same mine. Kim et al (2007) used the wet extraction method for two reasons; 1) they wanted to process large quantities of quartz from underground samples to measure ^{14}C and 2) they wanted to make separate measurements of the ^{14}C activity in the CO and CO$_2$ phases, as this information is useful in determining the contamination by environmental ^{14}C. This study is the first to measure *in situ* ^{14}C in sub surface samples. Kim et al., 2007 showed that the ^{14}C activities were significantly greater (by factors of 2-3), especially in samples of depths <200 g cm^{-2} (Kim *et al*., 2007). The excess ^{14}C measured was probably as a result of capture of thermal neutrons in nitrogen present in the fluid inclusions in quartz.

Cosmic-rays interact with all solid objects in the solar system to produce radioactivity, from dust grains and meteorites to planetary bodies. Beside the well known production of radiocarbon in the terrestrial atmosphere, spallation reactions of galactic and solar cosmic-ray particles on oxygen and silicon can result in the formation of many radionuclides. These high energy reactions differ from those associated with the atmospheric

production of ^{14}C due to thermal neutron capture by nitrogen. This information allowed studies into the level of galactic and solar cosmic ray particles in lunar samples, which can then be used to calculate the production, and variations, of solar cosmic-rays in the past (Fink *et al.*, 1998; Jull *et al.*, 1998a). The development of AMS permitted the measurement of ^{14}C in millimetre thick slices of rock to calculate production rates and the depth dependence on ^{14}C production (Jull *et al.*, 1992, 1998). There are three extra-terrestrial sources of ^{14}C observed in lunar samples: 1) production by nuclear reactions induced by galactic and solar cosmic-ray particles, 2) implantation by solar wind and 3) solar energetic particles (Jull *et al.*, 2000). One of the more interesting lunar extra-terrestrial applications was to look at the ^{14}C implanted on the surface of the moon in soil grains at a depth by the solar wind, which can have a speed of approx 450 km s^{-1}, to provide information on the nuclear reactions on the surface of the sun (Lal and Jull, 2001). Jull *et al.* (2000) present results which show that the ^{14}C/H ratio in the solar wind is between 0.4 –0.8 x 10^{-14}, assuming that the excess ^{14}C in the lunar regolith (above that produced by solar and galactic cosmic radiation) comes from the solar wind (Lal and Jull, 2001).

There are other examples of applications using *in situ* ^{14}C such as in meteorites which fall equally all around the world and have been recovered from many parts of the planet (Halliday *et al.,* 1989). The measurement on meteorites has improved from the early work of Suess and Wanke (1962) and Goel and Kohman (1962), who used 10 -100 g of sample analysed by ^{14}C decay counting. Now, researchers can use much smaller quantities of sample (0.1-0.7 g) and measure the ^{14}C by AMS (Jull *et al.*, 1989b, 1990, 1994, 1995). The study of terrestrial ages of meteorites provides information concerning the storage and weathering of meteorites and the study of fall times and terrestrial age. One of the most useful radionuclides for many meteorite collection areas is ^{14}C, as summarised by Jull *et al* (1990, 1998). In some cases, the terrestrial age

of the sample is at the limit of detection for ^{14}C and another isotope, such as ^{36}Cl, is used to calculate the age of the meteorite.

From the above discussion it is obvious that considerable progress has been made in the development of *in situ* ^{14}C measurement over the past two decades. The ultimate aim of this present study is to develop an extraction system that can be used routinely for the study of surface exposure dating to complement our existing capabilities for the measurement of ^{3}He, ^{10}Be, ^{21}Ne, ^{26}Al and ^{36}Cl (Freeman *et al*., 2004, 2007).

CHAPTER 2

METHODS

2.1. Quartz Preparation for *in situ* ^{14}C measurements

One of the most important stages of any applied research program is the selection, collection and pre-treatment of the samples to be analysed. In this study, a routine separation procedure for quartz was required that was capable of producing large quantities of clean quartz from different types of rocks and soils. Most of the published methods are based on the work of Kohl and Nishiizumi (1992) who developed a method for cleaning large quantities for use in the measurement of ^{10}Be and ^{26}Al. However, this method could be applied to the analysis of other *in situ* cosmic ray produced nuclides such as ^{14}C. During the *in situ* ^{14}C research undertaken at SUERC, three methods, were used to produce quartz suitable for analysis.

2.1.1. Kohl and Nishiizumi Method

The rocks were crushed using a jaw crusher and then ground to obtain predominantly mono minerallic grains of as large a size as possible. In most cases this was ≤ 700 µm. The ground sample was then heated in 1:1 HCl with 0.03% H_2O_2 (1 g sample per 10 ml) to dissolve any carbonates and iron oxides present. The residue was then washed several times with deionised water, and the fines discarded with the rinse water. The HCl treated powder was then leached with a dilute HF-HNO$_3$ mixture to dissolve the clays, feldspars and other silicate minerals. 7.5 g of this sample were added per litre of 1% HF-1% HNO$_3$. Leaching consisted of agitating the acid sample mixture for 9 hr in an ultrasonic bath heated to 95ºC. The leachate was discarded, the samples rinsed several times in deionised H_2O and then dried. Fines were discarded with the rinse water. The acid leach was repeated as necessary, usually to reduce the Al

content in the sample which is highly enriched in quartz, (between two to four times) and also removes feldspars and other high Al minerals from the sample. The acid strength was reduced in the second to fourth leaches.

2.1.2. The Edinburgh Method

The quartz samples used in our earlier study (Naysmith *et al.*, 2004) were prepared at the University of Edinburgh using the following pre-treatment method. The method used in the Edinburgh Laboratory is similar to that of Kohl and Nishiizumi (1992) although the ultrasonic bath used to clean the quartz was only heated to 30ºC and a 2% HF–HNO_3 acid mixture was used.

Before commencing the chemical pre-treatment, the quartz samples were crushed and sieved to 250-500 µm, they were then wet sieved in a 250 µm mesh sieve to remove fines and then oven dried at 50°C. Eight grams of sample were added to1 litre of 2% HF and 2% HNO_3; the mixture was sonically cleaned for 12-18 hrs at 30°C and rinsed with deionised water. This process was repeated four times, the sample rinsed five times in deionised water and then dried at 50°C. During the pre-treatment stages the quartz samples can adsorb a small amount of atmospheric CO_2, therefore, to aid the removal of this adsorbed CO_2, the samples were sonically cleaned in a 1:1 mixture of deionised water and HNO_3 for 30 min and then left in the acid for a further 90 min before being filtered and placed in a vacuum oven at 50°C overnight to dry (Bierman *et al.,* 2002). This method has been used to clean quartz samples at Edinburgh University when analysing for ^{10}Be and ^{26}Al and tests have shown exceptional quality resulting in aluminium concentrations of 100-200 ppm, which is extremely clean (Phillips *et al*., 2006).

The quartz samples for this study have been prepared in-house and the method is summarised below.

2.1.3. SUERC Method

In the SUERC method, 100-200 g of rough quartz-containing rock which had been crushed and sieved to 500 µm was weighed out and the weight. Recorded. The quartz was then added to a 2 litre plastic bottle together with 950 ml of 18 MOhm water. Once the quartz was mixed with the water 50 ml 40% specified grade hydrofluoric acid was added before the closed bottle was transferred to a shaker table where it was shaken at a medium speed setting (170 rpm) for 24-48 hrs. On completion, the hydrofluoric acid was decanted cautiously in a fume cupboard into a neutralisation tank. The quartz sample was then rinsed several times with 18 MOhm water and the solution again transferred to the neutralisation tank in the fume cupboard. The pH was checked after the third rinse and the rinsing process continued until the pH of the sample solution reached pH 6. The above HF etching procedure was repeated a further 4 times to improve the purity of the quartz sample. Following the third etching step, the purity of the quartz grains was checked under a microscope (but not necessarily after each etching from the third step onwards). During the 4th etching Certified grade hydrofluoric acid was used instead of Specified grade to improve the quality of the cleaned quartz.

To check the quality of the quartz pre-treatment the sample can be analysed for Al with the target value being 100-200 ppm.

Once the sample has been prepared to be measured for *in situ* ^{14}C there is one final step before the sample is ready to be placed in the system. The sample is placed in a solution of 1:1 HNO_3 and deionised water at room temperature and placed in a sonic bath for 30 min. The sample is then left in the bath for a further 90 min prior to being dried in an oven at 50ºC. This step is important as it reduces the amount of contamination on the samples as a result of handling and surface exposure of the quartz to

atmospheric contamination (Lifton, 1997; Barker and Torkelson, 1975). Lifton managed to reduce the contamination to non detectable levels (<8.32 x 10^3 atoms g^{-1} SiO_2) and is now able to store his quartz samples in air prior to the extraction process beginning.

2.2. Vacuum System

The design of the vacuum system for extracting *in situ* ^{14}C from quartz is based on the working system built by Lifton (1997) at the University of Arizona. The vacuum system used in this study was built using glass and a turbo pump backed by a diaphragm pump to eliminate the possibility of back streaming of oil vapour from the normal rotary backing pump or oil filled diffusion pumps. A schematic diagram of the vacuum system can be seen in Figure 4. The vacuum system can be split into three parts: 1) combustion and CO_2 collection, 2) CO_2 purification and measurement and 3) graphitisation.

2.3. Combustion and CO_2 Collection Section

The combustion and CO_2 collection section is made up with two furnaces, a re-circulating pump and three spiral traps for gas collection. The first stage in the combustion process is the preparation of a 65 cm length of 41 mm o.d. quartz sleeve tubing by heating the tube (using a glass-blowers hand torch) thoroughly in air for several minutes to burn off any surface contamination before it is inserted into the Mullite furnace. It is important not to handle the quartz tubing as this can add contamination, therefore gloves and stainless steel tongs are required to hold the quartz tube. An alumina boat (internal dimensions 135 mm length x 13 mm width x 17 mm depth) is taken and cleaned using a jet of compressed air before 20 g of $LiBO_2$ are placed into it before being inserted into the quartz sleeve inside the Mullite furnace. The quartz sleeve is used to protect the furnace from attack from the effects of $Li BO_2$ volatilization on the Mullite tube. The ultra clean quartz sleeve and sample boat which enter the Mullite furnace are

shown in Figure 5 (upper) together with a quartz sleeve and boat which have just been removed from the furnace (Figure 5 - lower).
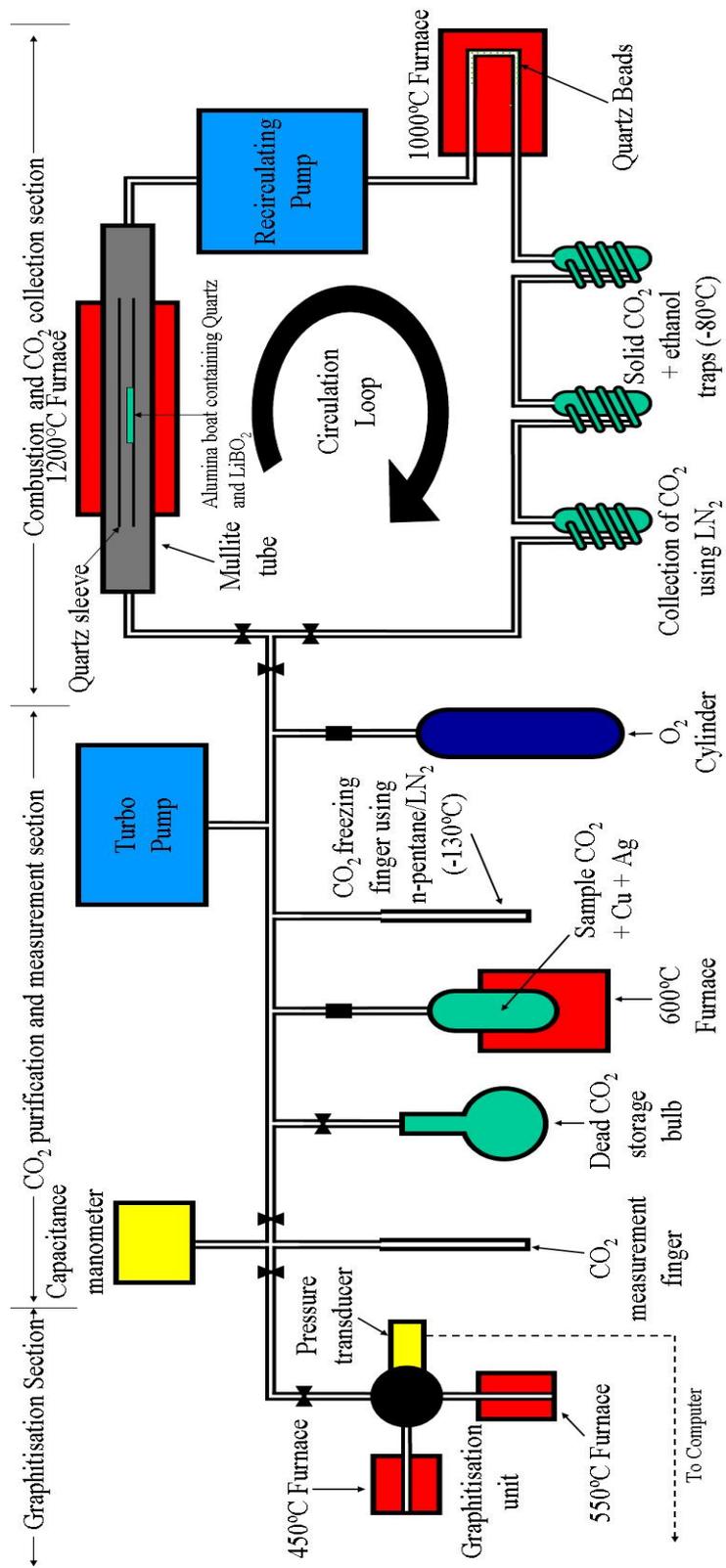
Figure 4: SUERC *in situ* extraction system
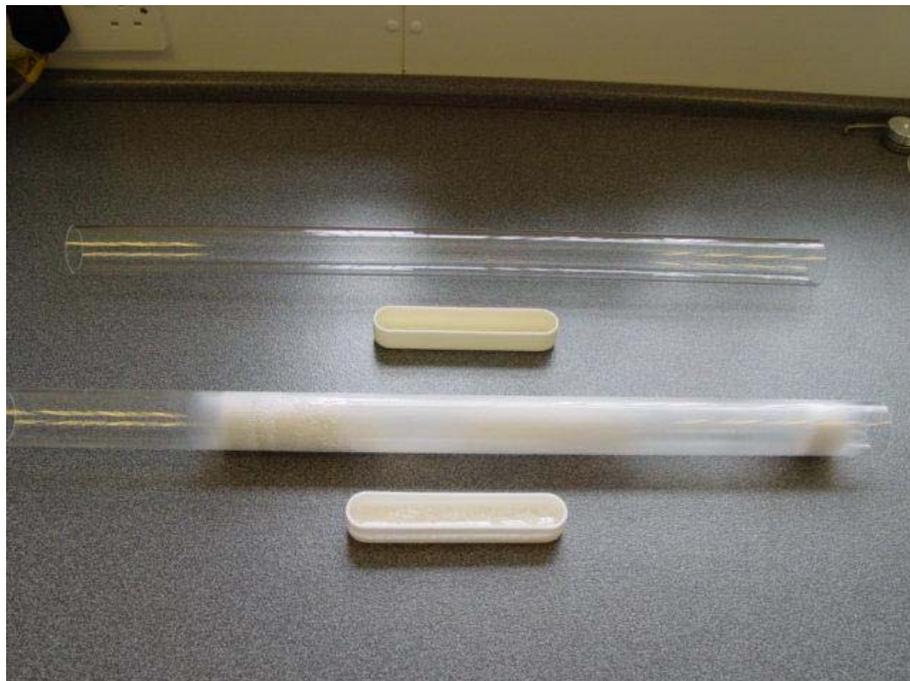
Figure 5: Quartz sleeve before (upper) and after (lower) the combustion stage

The sample boat is made of alumina (Al_2O_3) and is also itself attacked by the $LiBO_2$ just above the melt meniscus as shown in Figure 5. Figure 6 is a photograph which illustrates the effect of the $LiBO_2$ attack on the quartz sleeve after combustion and shows that the sleeve can only be used for one sample.

The combustion section of the vacuum system is dominated by the furnace which must be capable of reaching temperatures of 1200ºC. A Mullite (60% Al_2O_3, 40% SiO_2) tube was selected for use as the base of the furnace and this was connected to the vacuum system using a uranium glass capable of joining pyrex glass to the Mullite. Both ends of the tube were fitted with 'O' ring flanges to provide easy access for the quartz sleeve and the sample boat. Mullite was selected due to its performance in collecting small quantities of CO_2 from stepped heating

procedures (Des Maris, 1983; Des Marais and Moore, 1984). The heating part of the furnace was supplied by Watlow and comes in two identical
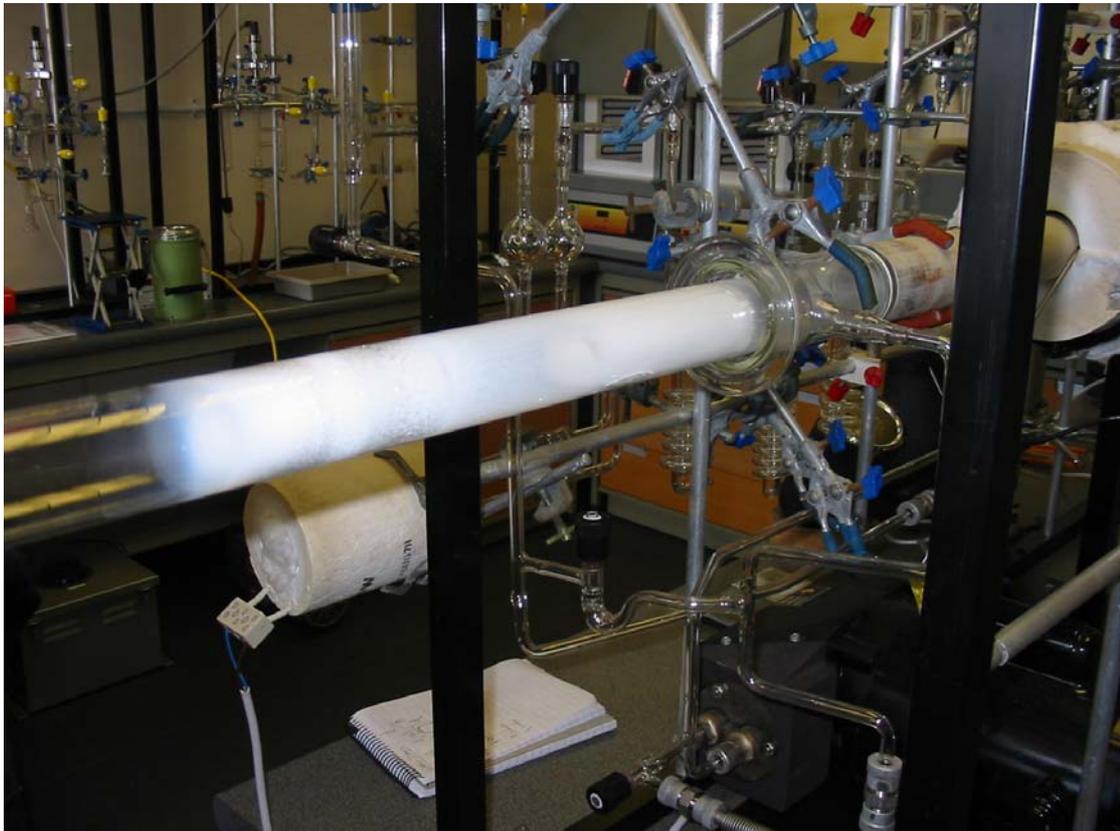
Figure 6: Quartz sleeve being removed from the furnace after combustion

halves which were rewired with tungsten to ensure the ability to reach the required temperature. The combustion procedures used on the quartz samples follow the stepped combustion procedures and systems developed by Des Marais for quantitatively extracting very small quantities of CO_2 from extraterrestrial samples and submarine basaltic glasses (Des Marais, 1983; Des Marais and Moore, 1984). The Des Marais method combusted small quantities of organic samples using a stepped combustion process which re-circulated approximately 30-40 mbar of ultra high purity oxygen around a resistance furnace capable of reaching 1700ºC. Pure quartz has a melting point of 1610ºC to 1730ºC however, the Mullite furnace used softens at 1325ºC therefore, a method of lowering the melting point of quartz is required. Lifton *et al.* (2001) experimented with different fluxing agents and variable mixtures before deciding to use

$LiBO_2$ which has a melting point of 845ºC. By using $LiBO_2$ in the ratio of 4:1 to the weight of quartz it is possible to use the Mullite tube as the centre core of the furnace as the melting point of quartz is reduced sufficiently. The combustion section of the vacuum system is shown in Figure 7. The main furnace is in the middle of the photograph with the three spiral traps in front of it. At the extreme left hand side is the UHP oxygen cylinder and the smaller quartz beads furnace is on the extreme right hand side.

Figure 7: The combustion section of the *in situ* vacuum system

A re-circulating pump (the black pump in Figure 7) was used to pass the gases produced in the furnace from the quartz/$LiBO_2$ through a second furnace heated to 1050ºC. This second furnace is made up from a quartz 'U' tube filled with 3 mm fused quartz beads. During combustion, not all the carbon is converted to CO_2, however, passing the gases through the second furnace ensures that all the carbon species generated are converted into CO_2. The gases are then passed through three cooled spiral traps - the first two are used to cryogenically collect the water vapour

from the sample while the third trap collects the CO_2. The first two traps are made up of a mixture of solid CO_2 and ethanol to give a temperature of -80ºC which traps out any water generated from the combustion process. The third trap uses LN_2 at a temperature of -196ºC, to collect the CO_2 from the gases which are circulated around the combustion loop. The ultra high purity oxygen is stored in a stainless steel cylinder which is attached to the vacuum system. For every combustion step a new fill of 30-40 mbar of oxygen is taken from the cylinder.

2.4. Purification and Measurement Section

After the CO_2 that was generated at 1050ºC has been collected, it must be purified as it will contain other gases which could result in graphite failure (also, the volume of CO_2 generated must be accurately known for the calculation of the number of ^{14}C atoms). The gases produced during combustion are a mixture of CO_2, SO_2, halides and oxides of nitrogen as a result of fluid inclusions trapped in the lattice of the quartz samples. The purification procedures used to clean up the CO_2 are: 1) passing the gas through a *n*-pentane/liquid nitrogen trap which will give a temperature of -130ºC, to remove SO_2 and water vapour from the CO_2, 2) combusting the CO_2 in a quartz combustion tube containing CuO and Ag at 500ºC to remove halogens from the gas sample and 3) collect the CO_2 from the quartz tube as it passes over an *n*-pentane trap/liquid nitrogen trap (-130ºC) to remove any traces of moisture picked up in the last clean up stage. An attempt was made to graphitise some CO_2 samples without running the clean up procedure but these samples failed to make graphite due to the impurities in the gas.

Once the CO_2 has passed through the clean up stages the gas has to be measured using a temperature corrected capacitance manometer attached to a finger with a known volume, which is shown in Figure 8. This is very important as the volume of the CO_2 generated from a single combustion has to be accurately determined. To calibrate the finger on

the *in situ* line, a known weight of Analar $CaCO_3$, was hydrolysed with HCl to produce a known volume of CO_2 which can be used to calculate the volume of the finger using a capacitance manometer.   When the capacitance manometer is open to atmosphere the reading is recorded to be used in the calculation to determine the volume of the finger.
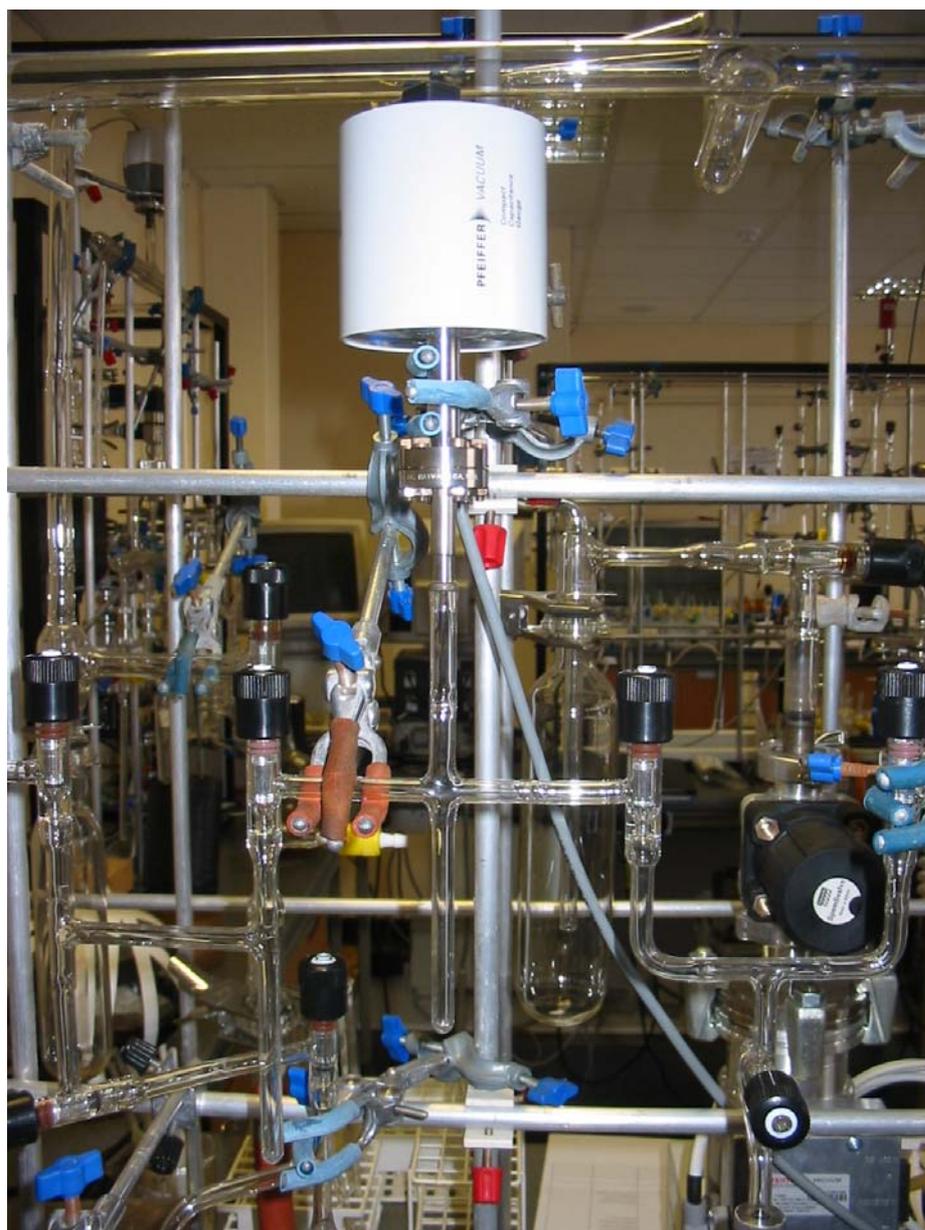
Figure 8: The capacitance manometer and measuring finger

Figure 9 shows the hydrolysis unit used to generate CO_2 from $CaCO_3$, it can be split in to three parts:- 1) the top, which has a vacuum stopcock and a rubber septum, 2) 9 mm cajon fitting and 3) the reaction tube. The accurately weighed $CaCO_3$ is placed into the bottom of the reaction tube; it is then connected to the top piece using the 9 mm cajon fitting and attached to the vacuum line. The hydrolysis unit is then pumped down to 10^{-5} mbar and 4 ml of HCl are added to the unit using a syringe through the rubber septum. Once the reaction is complete the stopcock is opened and the CO_2 passed through a slush trap (solid CO_2 and methanol mixture at $-80^{\circ}C$) to trap out the water and then the CO_2 is collected in a LN_2 trap ($-196^{\circ}C$). The system is then pumped to 10^{-5} and the CO_2 transferred to the measurement finger to record the pressure of CO_2 obtained.
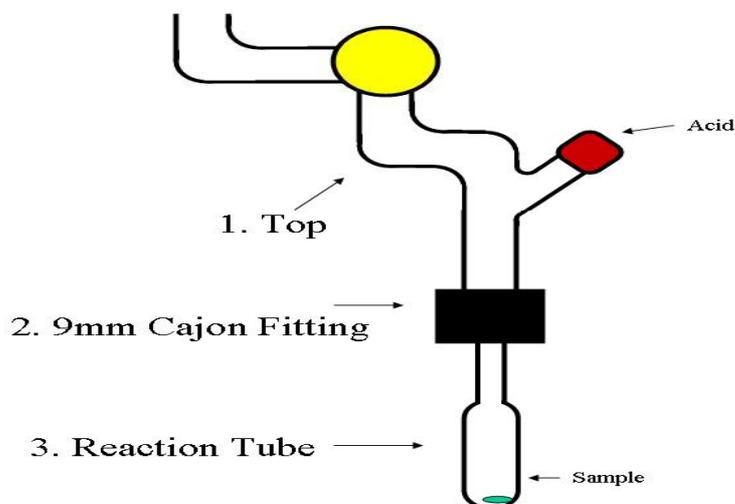
Figure 9: Hydrolysis unit

2.5. Calculations

The first step of the calculation to calibrate the finger volume on the *in situ* vacuum line is to determine the volume occupied by one mole of CO_2 gas at 25ºC using the following standard equation:-

$$PV = nRT$$

where
  P = Pressure in KNm^{-2} (1 Atmosphere is 101.325 KNm^{-2})
  V = Volume in litres (dm^3)
  n = Number of moles
  R = Gas constant (8.31415 $JK^{-1} mol^{-1}$)
  T = Temperature in degrees Kelvin (0ºC = 273.15ºK)

which can be re-arranged thus:-

$$V = nRT/P$$

$$ie.\ V= 1*8.31415*298.15/101.325$$
$$= 24.464\ litres$$

to show that 1 mole of CO_2 at 25ºC is equivalent to 24.464 litres of gas.

To ascertain the volume of the gas collection finger on the *in situ* line, 0.086 g of Analar grade $CaCO_3$ was accurately weighed and reacted with 4 ml of 1M HCl in the apparatus shown in Figure 9. The CO_2 generated was then collected and transferred to the collection finger and a note taken of the pressure reading showing on the capacitance manometer connected to the line. This pressure reading was then used to calculate the volume of the collection finger as follows:

Moles of $CaCO_3$ used = measured weight/Mol. Wt of $CaCO_3$

ie. 0.086/100.09

= 0.000859

= 0.000859 moles $CaCO_3$ used in the reaction

Vol. of gas generated = mol. $CaCO_3$ used * vol.1 mol. of CO_2 gas at 25ºC

ie. 0.000859 * 24464 ml

21.020 ml CO_2 generated

Vol. of the collection finger = Vol. gas generated * (Pressure reading atmosphere/Pressure reading on the gauge)

ie. 21.020 * 1000/969

= 21.693 ml

As the graphitisation process requires 1 ml of CO_2 gas to be converted to graphite these figures can be used to calculate the required reading on the capacitance manometer (*ie.* units per ml) as follows:

Units per 1 ml gas = Gauge reading at atmosphere

Collection finger volume

ie. 1000/21.693

= 46.098 units

Therefore to ensure that 1 ml of CO_2 is measured out for graphitisation requires the capacitance manometer to reach a value of 46.099. Table 8 presents the results for three attempts to calibrate the volume of the *in situ*

finger. An average of the three tests was used as the reading for 1 ml of CO_2 on the capacitance manometer.

	Test 1	**Test 2**	**Test 3**
Wt. of $CaCO_3$ (g)	0.086	0.087	0.088
Moles of $CaCO_3$	0.000859	0.000869	0.000879
Vol. gas generated (ml)	21.020	21.265	21.509
Pressure Reading	969	980	994
Finger Volume	21.693	21.699	21.639
Units per 1ml	46.099	46.086	46.213
Average		46.133	

Table 8: Results of $CaCO_3$ hydrolysis for finger calibration

2.6. Graphitisation Section

Figure 10 shows the main components of the graphite and measurement section of the extraction system. The procedure for making graphite is based on that described by Slota *et al.* (1987) which employs zinc and iron powder to reduce the CO_2 to C. The decomposition reaction of CO takes place as shown in the following equation.

$$2CO \underset{\leftarrow}{\rightarrow} CO_2 + C_{(gr)}$$

If the carbon is introduced as CO_2, and is reduced to CO using hot Zn, any CO formed due to the above reaction is then reduced to C by the hot Fe, ensuring that the reaction will proceed in one direction. The two reactions that take place in the conversion of CO_2 to graphite are:- 1) CO_2 is reduced to CO over Zn at 450ºC and 2) the CO disproportionates to graphite over Fe at 550ºC. All the graphite samples prepared during this study used a ratio of 2:1 iron:carbon. To achieve this, 2 mg of iron were

carefully weighed out into a 12.5 cm long, 6 mm OD closed-end quartz tube that had been pre-combusted at 500°C to remove any carbon contamination. In addition, 65-80 mg of zinc powder were placed into a similar quartz tube of 6 mm OD and 16.5 cm length. In the *in situ* system, the reaction is monitored using a pressure transducer interfaced to a computer and using in house software to display the reduction in pressure. Only samples that exceeded 90% conversion yield were accepted for measurement. The graphite production unit is an integral part of the extraction system (Figure 10) therefore, only *in situ* samples were run on this unit. This was undertaken in an attempt to eliminate potential memory effects from other carbon samples and to minimise gas handling. Once the graphite has been made, it is stored in a glass vial. It is pressed into an aluminium cathode (at 160 psi) immediately prior to AMS measurement.
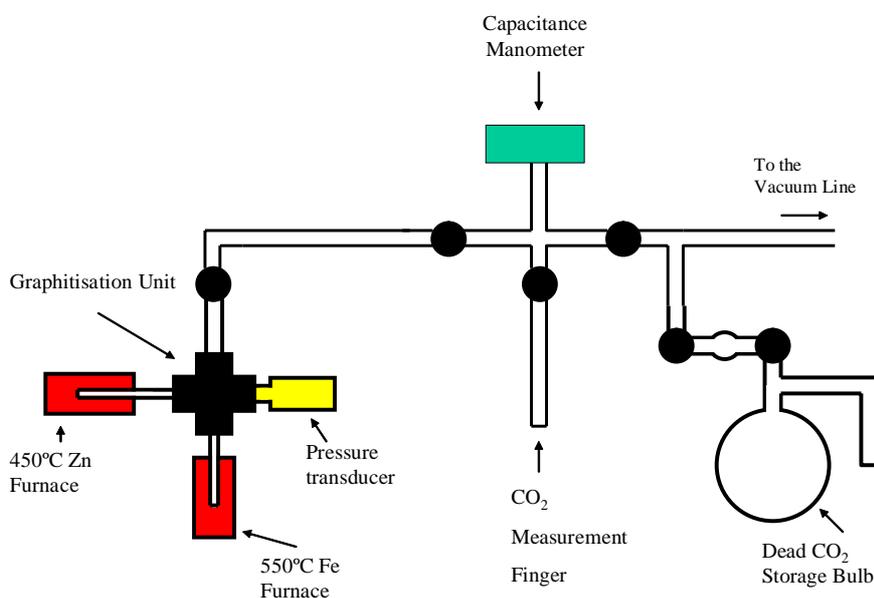
Figure 10: CO_2 measurement and graphite section of the extraction line

The quantities of CO_2 generated from quartz are very small therefore one of the first tests of the graphite system involved running a carbon mass test to ascertain the effects that measuring very small quantities of carbon

had on the AMS background. To do this, two litres of dead CO_2 were prepared from infinite age Icelandic doublespar by reacting it with HCl and collecting the CO_2 generated. The CO_2 is then stored in a glass bulb and attached to the *in situ* extraction line as shown in Figure 10. The next step involves the preparation of graphite targets from different quantities of carbon, ranging from 1.0 mg - 0.1 mg. The results are presented in Table 9 and shown in Figure 11.

GU No.	AA No.	CO_2 (mls)	Wt. Carbon (mg)	Graphite Yield (%)	F measured	Error (1σ)
10385	AA51186	1.994	1.015	98.6	0.0048	0.001
10386	AA51187	1.002	0.510	98.4	0.005	0.0012
10387	AA51188	0.802	0.408	97.9	0.0033	0.0011
10388	AA51189	0.603	0.307	97	0.0086	0.0011
10389	AA51190	0.402	0.204	98.6	0.0113	0.0012
10390	AA51191	0.198	0.101	94.7	0.0146	0.0013

Table 9: Graphite conversion test results
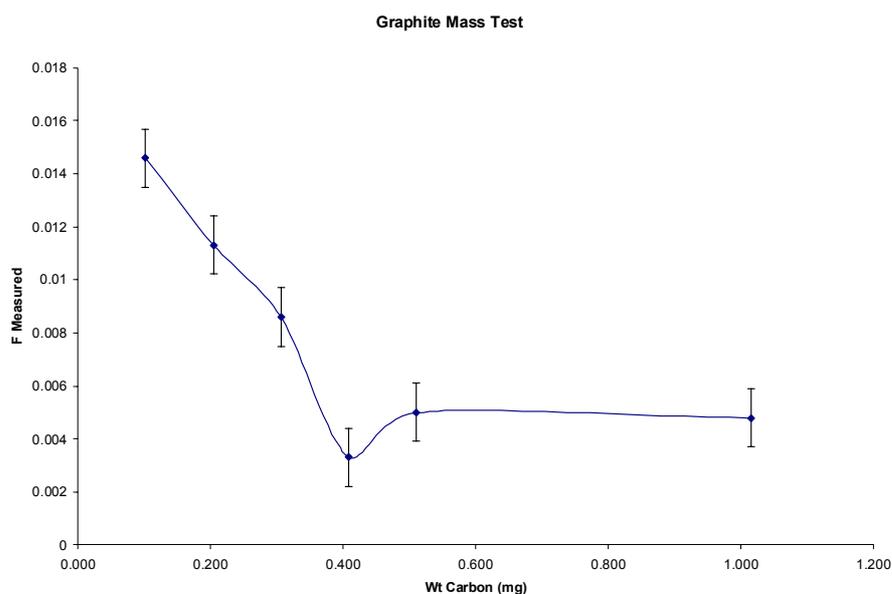
Figure 11: Change in background (F measured) against mass of graphite

Below approximately 0.4 mg C, as the weight of carbon decreases, the F measured value increases illustrating that, smaller samples have a greater chance of picking up contamination as they are prepared. The AA numbers in Table 9 indicate that the measurements were undertaken at the NSF facility in Arizona as the accelerator at East Kilbride was not operational at that time. Based on the information from this test it was decided to bulk up the CO_2 generated to 1ml using the Icelandic Doublespar CO_2 as the dilution gas. The measured F value at around 1ml of CO_2 (0.5 mg of C) has reached a constant value and will not add a large amount of contamination to the extraction line system blank. This is one of the most important factors in attempting to obtain a low system blank for the extraction procedure.

2.7. Improvements to SUERC *In Situ* System

The results from the initial NERC-funded study showed significant progress had been achieved in developing a method for extraction and measurement of *in situ* [14]C from quartz (Naysmith *et al.*, 2004). As discussed earlier, the main conclusions from this initial study were: 1) that larger volumes of CO_2 were generated from the PP-4 sample compared to the results of Lifton *et al.* (2001), and 2) when the PP-4 sample was measured, only around half the number of ^{14}C atoms were obtained compared to Lifton *et al.* (2001), perhaps as the result of a number of differences in the procedures used. The main focus of this further work is to take these conclusions and try to determine improvements to the extraction system that will lead to improved standards results.

Although the procedures and system developed at SUERC were based on those of Lifton there are several differences. The first was that Lifton used a second quartz sleeve, which had to be cleaned using a glassblower's torch to remove any atmospheric contamination and dust, that he used to remove the sample boat from the furnace. This meant that the main

sleeve remained in the furnace at all times and was only opened to the atmosphere when the quartz had to be added to the furnace. In the initial study, the main sleeve and the sample boat were removed together from the furnace when the sample quartz was being added to the boat. This has the effect of exposing the sleeve with its large surface area, to dust particles in the atmosphere of the laboratory. This material could contain ^{14}C contamination and this could have increased the volume of CO_2 generated at the combustion stage but the number of ^{14}C atom were less than expected. The next improvement made to the system was to change the Mullite furnace tube which had retained small quartz deposits from previous quartz combustions. These deposits were difficult to clean out of the system due to there being a flange at one end of the Mullite tube. When installing the new Mullite tube to the vacuum system, large 'O' joints (Figure 12) were installed at each end of the tube, making entry into the furnace from both ends possible. The large 'O' ring joint can be seen in Figure 12. It is made up of two glass flanges joined together with a viton 'O' ring placed in a groove on one of the flanges. The two flanges are held together with the large metal ring clamp which makes the glass to viton seal hold vacuum. At this point, the opportunity was taken to place heating tape at each end of the furnace. Lifton (pers. comm.) suggested that this reduced CO_2 adsorption onto the cold glass when the furnace was opened to the atmosphere. The heating tape is kept at a constant temperature of about 100ºC and remains on at all times during the extraction process.
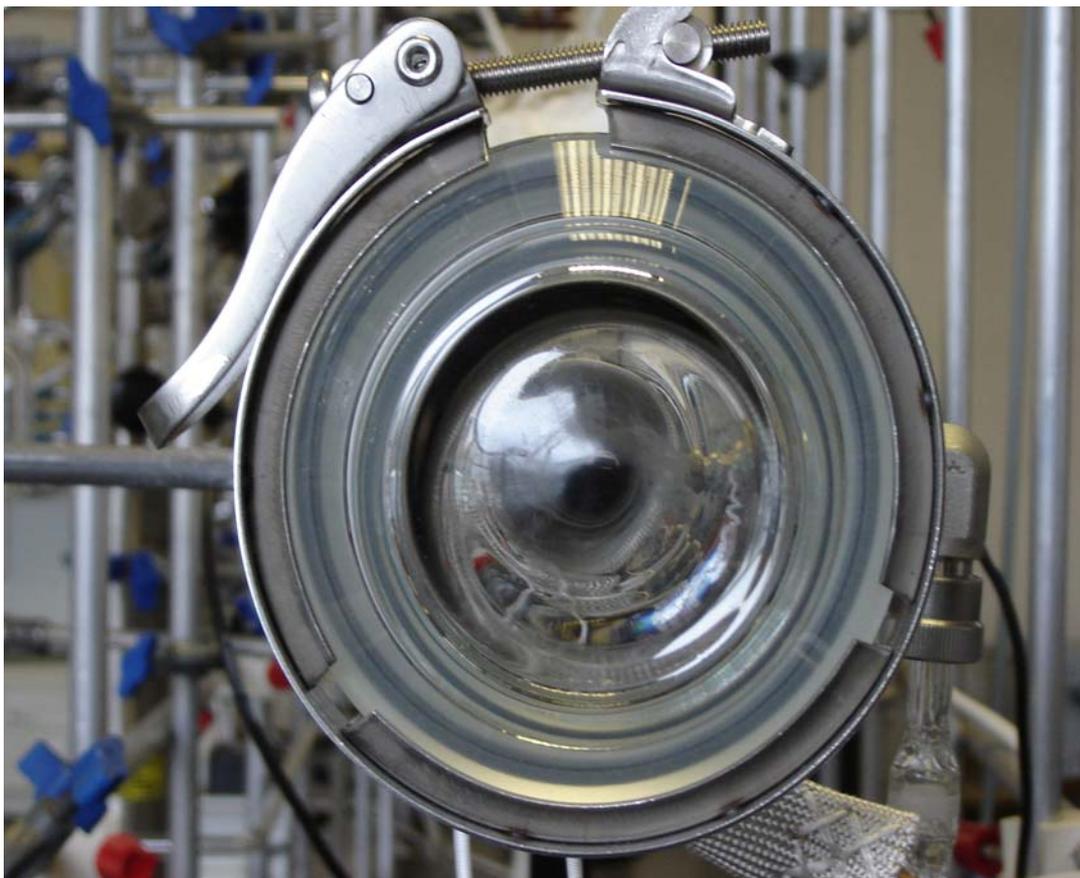
Figure 12: The new 'O' ring joint

Following the change of furnace, yield tests were run by putting a known volume of dead CO_2 from the gas storage bottle into the furnace prior to heating it to 1100ºC for 2-3 hr. 1 ml and 0.1 ml samples of CO_2 were used in this test, with the CO_2 circulated around the combustion section for 1 hour and then collected and measured. The results from this test are shown in Table 10. The results indicate that the new combustion tube is working well as the high percentage yields demonstrate.

Sample Number and Nominal Volume	Gauge Units Measured	Gauge Units Collected	% Yield
T1 (1 ml)	47.16	42.10	90
T2 (1 ml)	50.87	50.89	100
T3 (0.1 ml)	4.87	4.73	97
T4 (0.1 ml)	4.60	4.90	100
T5 (0.1 ml)	4.73	4.71	99.6
T6 (1 ml)	48.70	48.73	100.1

Table 10: Recovery tests results using 1 ml and 0.1 ml of CO_2

The next change was to the clean up procedure for the CO_2. In the previous study Naysmith *et al*. (2004) passed the CO_2 through *n*-pentane/liquid nitrogen traps (-130ºC) and then combusted the CO_2 in a small quartz tube using copper oxide and silver at 500ºC. The copper oxide used in this combustion could have added a very small amount of carbon to the CO_2 so it was decided to switch to the cleanup procedures used by Lifton (1997).   In an attempt to improve the CO_2 clean up procedure it was decided to use a pentane trap, followed by passing the CO_2 through a variable temperature trap and then finally, through a trap of copper and silver heated to 610°C. The variable temperature trap shown in Figure 13 was based on a design by Lifton who had based his design on those built by Des Marais (1978). The trap consisted of a metal cylinder with a column heater with a copper coil wound around it. The cylinder can be pumped down on the vacuum rig and then the whole trap placed into liquid nitrogen (-196°C) and the heater switched on to ensure that the temperature inside the trap is -150°C. The CO_2 is then passed through the copper coil which should trap out any impurities in the gas within the trap. Difficulties arose in trying to get the correct temperature inside the trap, possibly due to the thermal properties of the cylinder not allowing a stable temperature to be achieved inside the trap. As an

alternative, it was decided to use a trap combining a mixture of iso-pentane and liquid nitrogen to obtain the temperature of -150°C. All of the results reported in this thesis have been obtained using the amended procedures as described in this section.
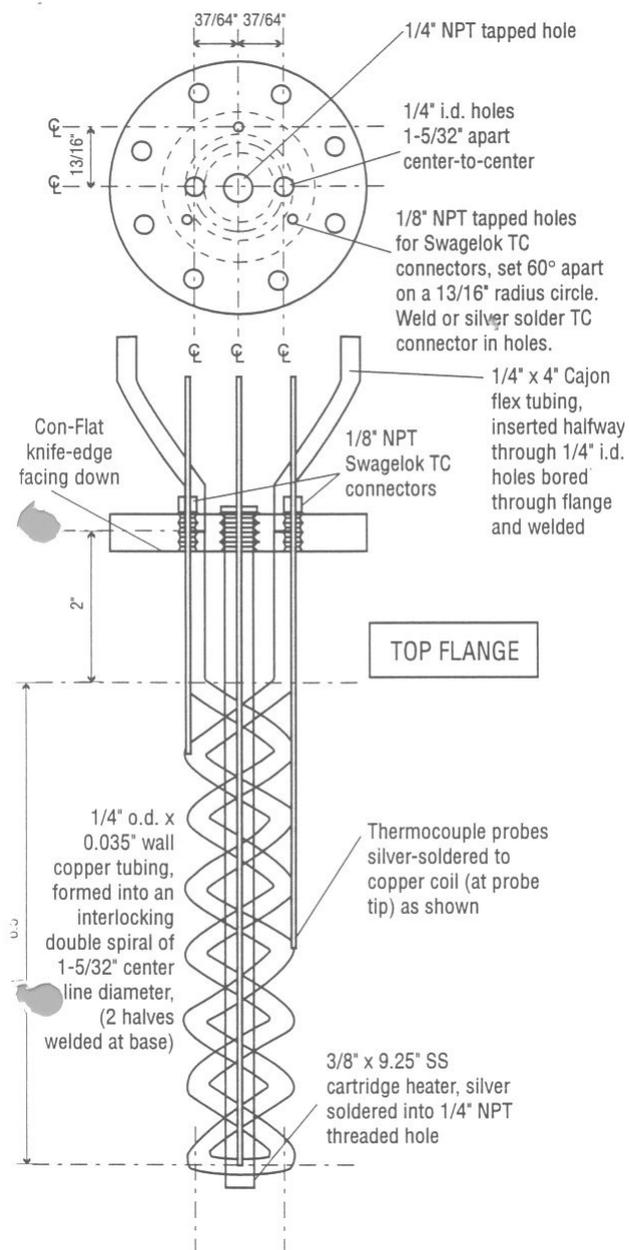
Figure 13: Variable temperature trap designed by Lifton (Lifton, 1997)

2.8. Combustion Recovery Test

Previous work (Naysmith *et al.*, 2004) highlighted a discrepancy in the results obtained during the analysis of Lifton's PP-4 sample with only half the number of ^{14}C atoms measured compared to other work (Lifton *et al.*, 2001). As a test of the new Mullite furnace and combustion section, a sample with a known activity (SRM-4990C oxalic acid) was combusted and measured against oxalic acids routinely prepared on the graphitization lines for measuring on the accelerator. To combust oxalic acid in the *in situ* line, 2.6 mg were put into a sample boat and placed in the furnace. The furnace was then pumped down slowly to stop the oxalic acid moving out of the boat and then the line was filled with oxygen to 40 mbar. The power was then switched on to the furnace to allow it to heat up to 1100º C, and the oxygen then circulated around the system, including the three spiral traps. The first two spiral traps trapped out water vapour using ethanol/solid CO_2 (-80ºC) while the CO_2 was collected in the third spiral trap using LN_2. Once the furnace had reached the required temperature it was left to re-circulate for 2 hours. The collected CO_2 was purified using pentane traps followed by passing the gas through a copper and silver trap heated to 600ºC, with the gas measured and the volume of CO_2 calculated. Table 11 shows the result obtained from combusting the oxalic acid in the *in situ* system as ^{14}C atoms and the measured value of atoms from sample T22 (oxalic acid primary standard) compared to the value for the primary standard. The ^{14}C atom recovery yield for this sample, compared to the standard was 98%, proving that most of the atoms released from the oxalic sample during combustion were collected - a significant improvement on the data presented previously in Naysmith *et al.* (2004), albeit that this was achieved using an organic sample. However, it did prove that actual collection of the ^{14}C atoms was not the issue.

Sample No	^{14}C atoms	Error (1σ)
T22	413.8 x 10^5	1.8 x 10^5
OX II	419.2 x 10^5	0.9 x10^5

Table 11: Single combusted Oxalic II vs. average Oxalic II standards

2.9. System Blanks

As discussed previously it was decided to use 1 ml of CO_2 for conversion to graphite for AMS measurement. After the combustion stage, the CO_2 was measured and the volume calculated and recorded. The gas was then made up to 1 ml by adding a volume of CO_2 made from Icelandic doublespar, which has no ^{14}C activity. A large volume of CO_2 was generated from Icelandic doublespar and then transferred into a glass storage bulb on the vacuum system. For every batch of samples that is measured on the AMS there are two doublespar targets to prove that the CO_2 stored in the storage bulb has no ^{14}C activity.

In the previous work (Naysmith *et al.*, 2004), the calculation of the system blank for the extraction system involved measuring out 1 ml of dead CO_2 and transferring it to the combustion system. The combustion system was then filled with oxygen, the CO_2 and oxygen allowed to mix, then the gas was "combusted" for 2-3 hours, and the CO_2 collected, purified, measured and the volume of CO_2 calculated. The ^{14}C from the system blank was only measured if the conversion of CO_2 to graphite was >90%. Changes in the method for calculating the system blank were made to ensure that all the steps in the extraction procedure were included. A new quartz sleeve was heated with a glassblower's torch and then placed in the furnace before a clean boat containing 20 g of $LiBO_2$ was placed in it. The system was then sealed and pumped down to 1x10^{-3} mbar before 40 mbar of oxygen were transferred into the furnace and heated to 1100ºC for 2 hr. Once the furnace was cooled down, a second smaller quartz sleeve was

cleaned and used to transfer the sample boat from the furnace, leaving the larger quartz sleeve in the furnace. At this point when running a sample, the boat would be removed and the quartz sample added to the boat, however, in the system blank test, the boat was removed but no quartz was added. The boat was then placed back inside the furnace using the small quartz sleeve, the furnace sealed and pumped down to 1×10^{-3} mbar before oxygen was added to allow the blank sample to be 'combusted' at 500ºC. The CO_2 from this combustion was pumped away after collection. The furnace was then left to cool before another aliquot of oxygen was added. A further combustion process, this time at a temperature of 1100ºC was undertaken, the CO_2 was collected, purified and the volume measured. This gas was then made up to 1 ml of CO_2 and converted to graphite to be measured as the system blank for the extraction system.

2.10.   SUERC AMS Systems

All samples were measured using a 5 MV pelletron from National Electrostatics Corporation (NEC). The 5 MV machine has two high intensity sputter ion sources allowing a high capacity for routine measurements of graphite samples on a 134 position wheel as well as a second gas ion source with a 40 position wheel. The 5 MV machine can now routinely measure ^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, ^{41}Ca and ^{129}I as part of its on-going research programs within the cosmogenic isotope research groups at SUERC (Freeman *et al.,* 2005). The local access to this machine has allowed the two on-site radiocarbon groups to increase their sample capacities, reduce turnaround times and produce reliable data from smaller samples. The measurement of cosmogenic *in situ* ^{14}C from quartz has become possible as smaller quantities of carbon (as low as 100 μg of carbon) can now be measured to 3‰ precision. The samples can be run at different currents (from 30 to 120 μA C$^-$) while maintaining a low background. ^{14}C background assessment is undertaken using graphite prepared from an interglacial wood sample and this produces a chemistry

background of ~55,000 yrs. A natural graphite sample from Ceylon has been measured on the accelerator and has produced a measured age of 80,000 yr proving the absence of ^{14}C in the detector. Routine radiocarbon samples are run at medium current (60 μA C$^-$) which will not allow for online δ^{13}C correction. This correction is made using off-line values from a conventional isotope ratio mass spectrometer.

Routine radiocarbon samples are run in sub-batches of 10 which include a primary standard, a background and a secondary standard (which is used to check the performance of the run). There are spaces for seven unknowns to be included in each sub-batch, and usually 10 -13 sub-batches will be placed in each wheel.

A batch of *in situ* samples included several different types of standards to generate the data required to complete the final calculation. 1 ml Oxalic Acid samples are used as the primary standard and 1 ml background samples are included to calculate the contamination correction factor to be applied to the data (Donahue *et al.*, 1990a). In the batch there will be 1 ml targets prepared from CO_2 gas from the bulb of dilution gas. These samples are run to check that the activity does not change. System blanks from the extraction system will be included in the batch to estimate a blank value for the extraction process. There will be unknown *in situ* samples and shielded quartz samples included in the batch. There will also be some of our radiocarbon in-house standards included in the batch to check the performance of the accelerator during the running of the batch.

2.11.   Summary of Extraction Method

In summary, the routine for extracting CO_2 from a quartz sample in this study is based on Lifton *et al.* (2001), and the main points are outlined in Figure 14 below:-

Day One	Day Two	Day Three
Heat a quartz sleeve to >800°C with a glassblowers torch. Place the sleeve inside the Mullite furnace. Clean an Al_2O_3 sample boat with compressed oxygen, add 20 g $LiBO_2$ and place in the furnace. Heat the furnace to 150°C and pump using the diaphragm pump to 10^{-1} mbar and then switch on the turbo pump. This can take about 2-3 hours. Collect the water and other gases in a LN_2 trap. Melt $LiBO_2$ in Ultra High Purity (UHP) O_2 at 1100°C for 1 hour. Allow to cool overnight.	Remove the sample boat from the furnace. Add 5 g of quartz to the boat. Return the boat to the furnace. Heat the furnace to 150°C and start pumping the system until 10^{-1} mbar then switch on the turbo pump. This can take about 2-3 hours. Add 30-40 mbar UHP O_2 and heat to 500°C, collecting the CO_2 for 1 hour. Allow to cool overnight.	Add ultra high purity UHP O_2 and then heat to 1100°C for 3 hours collecting the CO_2. Cryogenically clean the CO_2 using an *n*-pentane/liquid nitrogen trap (-130°C) and then pass the CO_2 gas over a quartz combustion tube containing Cu and Ag at 610°C to remove halogens from the gas sample. Pass the combusted CO_2 gas through an iso-pentane trap (-150°C). Measure the quantity of CO_2 produced and calculate the volume of gas generated. Add dead CO_2 to the gas to make the volume of CO_2 equal to 1 ml. Convert the CO_2 into graphite using the method of Slota *et al.* (1987). Remove graphite from the vacuum line.

Figure 14: CO_2 Extraction Process

This extraction process differs from the stepped combustion procedure of Des Marais and Moore (1984) as it involves two heating stages instead of three to extract the CO_2 from quartz. The first heating stage at 500°C

removes any atmospheric ^{14}C contamination still attached to the quartz sample after it has been cleaned using HNO_3. The gases from this step are then collected but are not cleaned or measured as these are not the gases of interest as *in situ* ^{14}C gases are released at higher temperatures (>500ºC to 1100ºC) (Lifton *et al.* 2001).

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Calculations

The samples in this study were measured on the SUERC 5MV accelerator, running at a current approaching 60 μA $^{12}C^-$ and employed the routinely-made off-line $\delta^{13}C$ for corrections to the measured $^{14}C/^{13}C$ ratio. Once the measurement of the batch of samples was completed, the raw data were manipulated using the National Electrostatics Corporation ABC program to produce $^{14}C/^{12}C$ and $^{14}C/^{13}C$ ratios for each sample. At SUERC, we use the $^{14}C/^{13}C$ ratio to calculate ^{14}C ages and ^{14}C activities for all of our unknown samples. The calculations are based on the methods of Donahue *et al.* (1990a), and use the following definitions:-

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Definitions

FF - the fractionation factor used to correct measured ratios for isotopic fractionation

f - the measured fraction modern of a background sample

Fm - the measured fraction modern with fractionation applied to both the sample and oxalic acid standard

F - Fm corrected for background

After the AMS laboratory has supplied a $^{14}C/^{13}C$ ratio for all the samples in the batch, the correct fraction modern (F) for each sample has to be calculated with its 1 sigma error. This calculation is completed in two steps:

3.1.1. Step One

Multiply the measured $^{14}C/^{13}C$ ratio by the Fractionation Factor (FF) to give Fm.

A fractionation factor is applied to the ^{14}C activity of all the samples to normalise them relative to -25‰ (theoretical value for 1890 wood). This is done by measuring the ^{13}C in the sample. The percentage depletion for an isotope is proportional to the difference in atomic mass, therefore, the depletion for ^{14}C is double that measured in the sample for ^{13}C. This is achieved by taking a small sub sample of CO_2 from every sample that is processed in the laboratory. The $^{13}C/^{12}C$ stable isotope ratio is reported in the $\delta^{13}C$ notation relative to V-PDB, where V-PDB is a Cretaceous belemnite from the Peedee formation in South Carolina and is the primary standard for $\delta^{13}C$ determinations. The CO_2 was measured on a VG SIRA 10 mass spectrometer which gives m/z 45/44 and 46/44 ratios for the CO_2 by comparing them against its standards. From the $^{13}C/^{12}C$ values determined from the measured 45/44 and 46/44 ratios, a $\delta^{13}C$ value can be calculated using the following equation.

$$\delta^{13}C = [^{13}C/^{12}C_{sample} / {}^{13}C/^{12}C_{standard} -1] \times 1000‰ \qquad (3.1)$$

Where

$\delta^{13}C$ = the $\delta^{13}C$ of the sample

$^{13}C/^{12}C_{sample}$ = the measured $^{13}C/^{12}C$ sample ratio

$^{13}C/^{12}C_{standard}$ = the measured $^{13}C/^{12}C$ standard ratio

Once the $\delta^{13}C$ value has been calculated, a fractionation factor (FF) may be determined using the following equation:

$$FF = \left(\frac{1 + \dfrac{-25}{1000}}{1 + \dfrac{\delta^{13}C_s}{1000}} \right) = \left(\frac{975}{1000 + \delta^{13}C_s} \right) \qquad (3.2)$$

Where

FF = Fractionation Factor

$$\delta^{13}C_s = \text{the } \delta^{13}C \text{ of the sample}$$

The error on the Fractionation Factor is calculated using the formula below:

$$1\sigma FF = \left(\frac{1\sigma \delta^{13}C_s}{1000 + \delta^{13}C_s} \right) * FF \qquad (3.3)$$

Where

$1\sigma FF$ = the 1 sigma error on the fractionation factor

FF = Fractionation Factor

$\delta^{13}C_s = \delta^{13}C$ of the sample.

$1\sigma\delta^{13}Cs$ = the 1 sigma error of the measured $\delta^{13}C$ of the sample taken from the mass spectrometer

To complete step one you now multiply the $^{14}C/^{13}C$ ratio by the fractionation factor and calculate the 1σ error and then calculate Fm and 1σ Fm using the following equations:

$$Fm = \left(\frac{\left(^{14}C/^{13}C\right)_S * \left(\frac{975}{\left(1000 + \delta^{13}C_S\right)} \right)}{0.7459 * \left(^{14}C/^{13}C\right)_{OxII} * \left(\frac{975}{\left(1000 + \delta^{13}C_{OxII}\right)} \right)} \right) \qquad (3.4)$$

Where

Fm = the measured fraction modern

$\delta^{13}C_s$ = the $\delta^{13}C$ of the sample

$\delta^{13}C_{OXII}$ = the $\delta^{13}C$ of the oxalic acid standard

$\left(^{14}C/^{13}C\right)_S$ = the measured $\left(^{14}C/^{13}C\right)$ ratio of the sample

$\left(^{14}C/^{13}C\right)_{OXII}$ = the measured $\left(^{14}C/^{13}C\right)$ ratio of the oxalic acid standard

The 1σ error associated with Fm is calculated using:

$$Fm1\sigma = Fm * \sqrt{\left(\frac{1\sigma({}^{14}C/{}^{13}C)s * FF}{({}^{14}C/{}^{13}C)s * FF}\right)^2 + \left(\frac{1\sigma({}^{14}C/{}^{13}C)_{Oxll} * FF}{({}^{14}C/{}^{13}C)_{Oxll} * FF}\right)^2} \qquad (3.5)$$

Where

Fm1σ = 1 sigma error in the calculation of Fm

Fm = the measured fraction modern

FF =– Fractionation Factor

$({}^{14}C/{}^{13}C)_S$ = the measured $^{14}C/^{13}C$ ratio of the sample

1σ $({}^{14}C/{}^{13}C)_S$ = the error on the $^{14}C/^{13}C$ ratio of the sample

$({}^{14}C/{}^{13}C)_{OXII}$ = the measured $^{14}C/^{13}C$ ratio of the oxalic acid standard

1σ $({}^{14}C/{}^{13}C)_{OXII}$ = the error on the $^{14}C/^{13}C$ ratio of the oxalic acid standard

3.1.2. Step Two

Calculate the Fraction Modern (F) by applying the contamination (background) correction equation (Donahue *et al.,* 1990a):

$$F=Fm(1+f) - f \qquad (3.6)$$

The second step in the calculation involves calculating F. The first part of this calculation is to determine f. Every batch of samples that is run on the accelerator includes a number of background samples prepared in our laboratory.   These background samples are put through the same chemical and extraction procedures as our unknown samples to try and quantify how much contamination is added to the sample during the processes. To calculate f, all the background samples are grouped together and used to calculate an apparent fraction modern of background, by using the measured $({}^{14}C/{}^{13}C)$ ratio of a background sample (or a mean of selected background sample ratios) and the

associated 1 sigma error. The formula to calculate f and the 1σ error are shown below:

$$f = \left| \frac{\left({}^{14}C/{}^{13}C\right)_{BK} * \left(\dfrac{975}{\left(1000 + \delta^{13}C_{BK}\right)} \right)}{0.7459 * \left({}^{14}C/{}^{13}C\right)_{OxII} * \left(\dfrac{975}{\left(1000 + \delta^{13}C_{OxII}\right)} \right)} \right|$$

(3.7)

Where

    f = the fraction modern of the background as measured

    $\delta^{13}C_{BK}$ = the $\delta^{13}C$ of the background

    $\delta^{13}C_{OXII}$ = the $\delta^{13}C$ of the oxalic acid standard

    $\left({}^{14}C/{}^{13}C\right)_{BK}$ = the measured $\left({}^{14}C/{}^{13}C\right)$ ratio of the background sample

    $\left({}^{14}C/{}^{13}C\right)_{OXII}$ = the measured $\left({}^{14}C/{}^{13}C\right)$ ratio for the oxalic acid standard

$$f1\sigma = \sqrt{\left(\frac{1\sigma \overline{\left({}^{14}C/{}^{13}C\right)_{BK} * FF}}{\left({}^{14}C/{}^{13}C\right)_{BK} * FF} \right)^2 + \left(\frac{1\sigma \left({}^{14}C/{}^{13}C\right)_{OxII} * FF}{\left({}^{14}C/{}^{13}C\right)_{OxII} * FF} \right)^2} * f$$

(3.8)

Where

    f1σ = 1 sigma error in the calculation of Fm

    f = the Fraction Modern of background as measured

    FF = Fractionation Factor

    $\left({}^{14}C/{}^{13}C\right)_{BK}$ = the measured $\left({}^{14}C/{}^{13}C\right)$ ratio of the background

    $1\sigma \left({}^{14}C/{}^{13}C\right)_{BK}$ = the error on the $\left({}^{14}C/{}^{13}C\right)$ ratio of the background

    $\left({}^{14}C/{}^{13}C\right)_{OXII}$ = the measured $\left({}^{14}C/{}^{13}C\right)$ ratio of the oxalic acid standard

    $1\sigma \left({}^{14}C/{}^{13}C\right)_{OXII}$ = the error on the $\left({}^{14}C/{}^{13}C\right)$ ratio of the oxalic acid standard

Once f has been calculated you can use the contamination correction equation (3.6) to calculate F.

In this study the data will be presented as the number of ^{14}C atoms from a single combustion for blanks and unknown samples. The calculation to determine the number of ^{14}C atoms in a blank sample is given below:

$$Blank\,N_{14} = \left(\frac{FA_{14}N_AV_S}{V_A} \right) \qquad (3.9)$$

Where

Blank N_{14} = number of ^{14}C atoms from a sample blank

F = the corrected fraction modern of the blank sample

A_{14} = fractional abundance of ^{14}C in modern carbon (1.177 x 10^{-12} for ^{14}C/^{12}C)

N_A = Avogadros number (6.023 x 10^{23})

V_S = volume of CO_2 collect in a combustion step

V_A = volume of 1mole of CO_2 at STP

To determine the number of ^{14}C atoms for an unknown sample the following equation is used:

$$N_{14} = \frac{\left(\dfrac{FA_{14}N_AV_S}{V_A} - B \right)}{M} \qquad (3.10)$$

Where

N_{14} = concentration of ^{14}C atoms from a combustion step

F = the corrected fraction modern (^{14}C/^{13}C ratio) of the unknown sample

A_{14} = fractional abundance of ^{14}C in modern carbon (1.177 x 10^{-12} for ^{14}C/^{12}C)

N_A = Avogadros number (6.023 x 10^{23})

V_S = the volume of CO_2 collected in a combustion step

V_A = volume of 1mole of CO_2 at STP

B = the number of ^{14}C atoms associated with the extraction blank

M = the sample mass in grams

To calculate the error for the number of ^{14}C atoms for a single combustion the following equation is used:

$$\sigma\,^{14}N = \frac{^{14}N \times 1\sigma F}{F}$$
(3.11)

Where
  $\sigma\,^{14}N$ = error on the number of atoms associated with one single combustion step

  ^{14}N = concentration of ^{14}C atoms from a combustion step

  $1\sigma F$ = error on the Fraction Modern

  F = the corrected fraction modern ($^{14}C/^{13}C$ ratio) of the unknown sample

3.2. Results

3.2.1. Quality Assurance Standards

As described in Chapter 2, known age/activity quality assurance (QA) standards are measured in each sample batch along with unknown *in situ* samples and shielded quartz samples. The samples used are from our radiocarbon in-house standards and are included in the batch to check the performance of the accelerator during the running of the batch. Table 12 shows the results for 1 ml Barley Mash samples presented as measured fraction modern (Fm). Barley Mash is used in the radiocarbon laboratory as an in-house standard because all the barley used in the distillation of whisky comes from a single year's growth. The Barley Mash sample has also been used as an intercomparison sample in the Third International

Radiocarbon Intercomparison (TIRI) program where a set of samples was sent to all the radiocarbon laboratories for measurement and the returned results used to calculate a consensus value. The Barley Mash was Sample A in TIRI and has a consensus value of 116.35 ± 0.0084 pmC (Scott, 2003). The average value for the four measured numbers presented here was 116.74 ± 0.40 (Table 12) and can be compared to both the TIRI consensus value and to our own laboratory average value of 116.47 ± 0.32 pmC which is an average value calculated over the last year of measurement in the radiocarbon laboratory.

SUERC No.	Sample Code	Fm $\pm$ 1σ
SUERC-3656	BBM-182	1.1704 ± 0.0023
SUERC-3665	BBM-203	1.1720 ±0.0039
SUERC-9550	BBM-411	1.1626 ± 0.0034
SUERC-9560	BBM-412	1.1615 ± 0.0025
	Average	**1.1674 ± 0.0040**

Table 12: Results for Barley Mash samples

The second QA sample used in the *in situ* study was a cellulose sample prepared in the radiocarbon laboratory from a Scots Pine collected from Ireland. The sample contains 40 growth rings from a sequence that was dendro-dated at Queens University, Belfast. This sample was used in the Fourth International Radiocarbon Intercomparison study (FIRI) as Sample I and has a consensus value of 4485 ± 5 years BP (Scott, 2003). The results in Table 13 are from 1 ml cellulose samples individually combusted (BC samples) and also 1 ml aliquots taken from a large combustion (BBC sample) which generated 5 litres of gas. The results are presented in age BP and are all within error of the FIRI consensus value.

SUERC No.	Sample Code	Age (BP) $\pm 1\sigma$
SUERC-3655	BBC-129	4478 ± 40
SUERC-3666	BBC-142	4507 ± 40
SUERC-9531	BC-528	4510 ± 35
SUERC-9541	BC-529	4480 ± 35
	Average	**4494 ± 19**

Table13: Results for Belfast Cellulose samples

3.2.2. Performance Results

Once the changes described in Chapter 2 were implemented, the vacuum system underwent a series of tests to monitor its performance. These tests were designed to provide confirmation of the level of background associated with all the processes in the system while investigating the effect of sample size on the results obtained. Firstly, in order to assess that the graphitisation section (Section 3) of the *in situ* vacuum system was generating realistic results, Doublespar blanks (*ie* CO_2 generated from Icelandic calcite) were analysed. Table 14 shows the results (as ^{14}C atoms) obtained from 1 ml samples of this CO_2 (taken from the reservoir), which were converted into graphite on the *in situ* line.

SUERC No.	Sample Code	Fm $\pm 1\sigma$	^{14}C Atoms (x10^5)
SUERC-3659	T9	0.0017 ± 0.0001	0.5105 ± 0.0300
SUERC-3662	T20	0.0018 ± 0.0001	0.5245 ± 0.0291
SUERC-9551	T32	0.0018 ± 0.0001	0.5321 ± 0.0296
SUERC-9552	T35	0.0008 ± 0.0001	0.2358 ± 0.0295
SUERC-9553	T38	0.0009 ± 0.0001	0.2710 ± 0.0301

Table 14: Results for 1 ml Doublespar blank samples

It is important to include 1 ml Doublespar blank samples in all ^{14}C *in situ* batches to check the activity of the bulk gas being used to make up the volume of CO_2 extracted from quartz samples to 1 ml. The average Fm value for the 1 ml Doublespar blank samples run in this study is 0.0014 ± 0.0001 which compares to 0.0014 ± 0.0004 for Doublespar samples run in the SUERC radiocarbon laboratory QA program, although the SUERC laboratory average is based on using 3 ml targets. There is a difference in the last two samples (T35 and T38) from the first three; the reason for this could be due to the improvements to the AMS system over the measuring period of this study.

Secondly, the effect of sample size was investigated by using both 1 ml and 0.1 ml volumes of Doublespar CO_2 gas. Each sample was circulated through the combustion section of the vacuum system in the presence of ultra high purity oxygen and then collected and measured before being converted into graphite. The results for the recovery tests are shown in Table 15 (as ^{14}C atoms) and indicate that approximately 100% recovery was achieved for the 1 ml samples (T6 and T7) with similar recoveries for the 0.1 ml samples (T18 and T19).

SUERC No.	Sample Code	Sample Vol. (ml)	Recovery %	Fm $\pm$ 1σ	^{14}C Atoms (x10^5)
SUERC-3657	T6	1	100.1	0.0025 $\pm$ 0.0001	0.7658 $\pm$ 0.0306
SUERC-3658	T7	1	100.7	0.0015 $\pm$ 0.0001	0.4600 $\pm$ 0.0307
SUERC-3560	T18	0.1	98.7	0.0012 $\pm$ 0.0001	0.3457 $\pm$ 0.0288
SUERC-3561	T19	0.1	99.1	0.0018 $\pm$ 0.0001	0.5183 $\pm$ 0.0288

Table 15: Results from recovery tests on 0.1 ml and 1 ml blank samples

The results from these tests illustrate that the level of contamination is not influenced by sample size as the smaller sized samples (T18 and T19) have comparable Fm results to those obtained for the larger 1 ml (T6 and T7) samples.   The Fm values are very similar for the two pairs and when

compared to those for the 1 ml Doublespar blanks (T9 and T20 from Table 14) run in the same batch on the accelerator, there is no difference between them.

The method used to extract system blanks for the vacuum system has been described previously in Chapter 2. Our procedure is now the same as that used by Lifton at the University of Arizona. The results for the system blanks (presented as ^{14}C atoms) are shown in Table 16. These system blanks are run in the absence of gas and provide an indication of potential contamination in all the sections of the vacuum system.

SUERC No.	Sample Code	CO$_2$ Volume (ml)	Fm $\pm$ 1σ	^{14}C Atoms (x10^5)
SUERC-9554	T33	0.082	0.0440 $\pm$ 0.0003	13.4123 $\pm$ 0.0992
SUERC-9555	T34	0.038	0.0154 $\pm$ 0.0002	4.5450 $\pm$ 0.0610
SUERC-9556	T36	0.017	0.0029 $\pm$ 0.0001	0.8371 $\pm$ 0.0246
SUERC-10319	T42	0.086	0.0263 $\pm$ 0.0004	7.6508 $\pm$ 0.1163
SUERC-10320	T43	0.079	0.0201 $\pm$ 0.0004	5.7674 $\pm$ 0.1148
SUERC-10346	T44	0.115	0.0467 $\pm$ 0.0006	13.6802 $\pm$ 0.1832

Table 16: Results for system blanks for the *in situ* system

The volume of CO$_2$ generated during a system blank run varied from 0.017 to 0.115 ml. This volume is directly related to the number of ^{14}C atoms measured, with the highest volume of CO$_2$ giving the largest number of ^{14}C atoms. The most likely origin of the variation in CO$_2$ produced within the system blank relates to the cleaning of the quartz tube which is placed inside the furnace as protection from attack by the Li BO$_2$. As described in Chapter 2, the quartz tube is heated with a glassblowers torch to >800°C in an attempt to remove any contamination. The variable CO$_2$ volumes could be a result of insufficient heating of both this, and the second smaller quartz tube which is used to transfer the sample boat into and out of the furnace. This may result in unburnt dust particles remaining attached to these tubes which can then release CO$_2$ during combustion.

At the beginning of this study a new Mullite tube was installed in the furnace, it was then pumped and heated to try and clean it before test samples were run through it. The results of the system blanks run through this new tube showed variable and often relatively high values for Fm. This trend was also seen in the initial study by Naysmith *et al.*, 2004 when 1 ml doublespar samples were "combusted" and then collected and converted into graphite to be measured on the AMS. However, eventually, the system blanks came down to a lower and more stable value. This suggests that the continuous running of the vacuum system with ultra-high-purity O_2 was slowly cleaning contaminant carbon from the line. It also demonstrated that great care must be taken to keep the line isolated from sources of contaminant carbon.

Table 17 compares the average value for the system blank (0.88 ± 0.09 ^{14}C atoms x 10^6) for this study with other results recorded in the literature. The system blank for this study is not as low as the systems in Arizona (Lifton *et al.*, 2001; Miller *et al.*, 2006) but is lower than that recorded by Yokoyama *et al.* (2004). It is difficult to compare the results from the literature as every system is different and all the extraction techniques vary. One of the main aims in developing this system was to achieve a low and constant blank. This work has shown that the system blank is low but not as constant as had been hoped and therefore more work is required.

Reference	^{14}C Atoms (x10^6)
Lifton *et al.*, 2001	0.15±0.01
Pigati *et al.*, 2007	0.24±0.01
Jull *et al.*, 1994	1.5±0.2
Yokoyama *et al.*, 2004	2.3±0.2
This study	0.88±0.09

Table 17: Results for system blanks from the literature

The main conclusions from the initial measurements and results for this new system were presented at the 18th International Radiocarbon Conference in New Zealand (Naysmith *et al.*, 2004) with the main positive conclusion being that the system we had designed, built and tested was capable of giving consistently low ^{14}C system blanks (see Chapter 1). However, on the negative side:- 1) the shielded and surface quartz samples that were analysed generated larger volumes of CO_2 than Lifton *et al.* (2001) and 2) the results from the surface quartz sample (PP-4) obtained from the University of Arizona and used as an in-house standard, only generated half the expected number of ^{14}C atoms. After the conference a number of important changes were made to the vacuum system as described in Chapter 2 and the main aim of this study was to assess the effectiveness of these changes and to report the new results.

To investigate the first of these conclusions the volume of CO_2 generated from samples of the Lake Bonneville PP-4 quartz during this and our previous study are presented as millilitres of CO_2 in Table 18. In this study (T39 – T41 and T45 – T48) the CO_2 volume generated is on average half that extracted in the previous study (PP-4-1 – PP-4-3). The reasons for this lower volume of CO_2 are potentially:- 1) improvements to the preparation and handling of the quartz tubes during the combustion stage, 2) placing heating tape onto the outside of the Mullite furnace and the glass joining the furnace to the vacuum system to minimise adsorption of CO_2 and 3) the new clean-up procedures for the CO_2 using a combination of an n-pentane (-130ºC) trap followed by a copper and silver trap which is heated to approx. 600ºC before passing the CO_2 through an iso-pentane trap (-150ºC). Passing the CO_2 through these traps ensures that most of the impurities are removed from the CO_2 before the gas is measured at the calibration finger. It is also possible that the clean up procedure in the previous study did not remove all the contaminants from the CO_2, which meant larger volumes of gas, were measured.

Sample No	Sample Code	CO_2 Volume (mls)
GU-11240	PP4-1	0.2537
GU-11241	PP4-2	0.1488
GU-11242	PP4-3	0.2176
SUERC-9557	T39	0.0965
SUERC-9558	T40	0.0555
SUERC-9561	T41	0.1171
SUERC-13047	T45	0.1117
SUERC-13048	T46	0.1061
SUERC-13054	T48	0.1054

Table 18: CO_2 volumes from Lake Bonneville PP-4 quartz samples

3.2.3 PP-4 Results

The second main conclusion from the previous study (Naysmith *et al*., 2004), was that the PP-4 only generated half the expected number of ^{14}C atoms compared to Lifton *et al*. (2001). To investigate this conclusion, more PP-4 quartz samples from Lake Bonneville Utah were analysed. Another batch of this sample was obtained from Lifton at the University of Arizona and the SiO_2 purified at SUERC.

The results obtained from running the PP-4 sample are shown in Table 19, with the results given in ^{14}C atoms g^{-1} SiO_2. These have been calculated using equation 13.10 to determine the number of atoms per sample.

However, before this calculation can be performed, a system blank is subtracted from the total number of atoms counted. The value employed was an average of the data from Table 16. While this is less than ideal, since there was still variability in these data, it was the best value available.

SUERC No.	Sample Code	$F \pm 1\sigma$	^{14}C Atoms $(g^{-1}SiO_2 x10^5)^*$
SUERC-9557	T39	0.0789 ± 0.0007	3.2020 ± 0.0424
SUERC-9561	T41	0.0793 ± 0.0005	3.2275 ± 0.0301
SUERC-13047	T45	0.0897 ± 0.0008	3.2921 ± 0.0449
SUERC-13048	T46	0.0815 ± 0.0007	3.1749 ± 0.0454
SUERC-13054	T48	0.0921 ± 0.0006	3.4069 ± 0.0442

Table 19: PP-4 results in ^{14}C atoms $g^{-1}SiO_2$ calculated using equation 3.10 (page 62).

(*Before being corrected for sample thickness, topographic shielding and a correction to pure SiO_2)

To calculate final numbers for the PP-4 quartz sample, the data have to be corrected for sample thickness, topographic shielding and purity of the SiO_2. When using a standard model for calculating cosmogenic nuclide production there is an assumption that the production is taking place below a horizontal planar surface. In actuality, many samples are collected from sloping surfaces, and many samples are in the vicinity of topographic irregularities which may block part of the otherwise incident cosmic radiation. The effects of these factors are usually termed shielding. The correction used for topographic shielding for the Lake Bonneville PP-4 sample is 1.0064 ± 0.0255 (Lifton, pers. comm.). The correction factor for the sample thickness (corrects the sample to the surface) is 1.0779 ± 0.0106 (Lifton, pers comm.). Major element analyses for SiO_2 purity calculation were not undertaken in this study although the same correction factor of 1.0027 ± 0.0266, as used by Miller *et al.* (2006), was employed. While there is an assumption here, the correction factor is small and a very similar SiO_2 cleanup process to that used by Lifton et al. (2001) and Miller et al. (2006) was employed. Once the F value has been calculated, these factors can be applied by multiplying the F value with each correction

factor in turn until the final number of ^{14}C atoms is calculated. The final numbers for PP-4 are presented in Table 20.

SUERC No.	Sample Code	F ± 1σ	^{14}C Atoms ($g^{-1}SiO_2x10^5$)
SUERC-9557	T39	0.0789 ± 0.0007	3.4765 ± 0.0424
SUERC-9561	T41	0.0793 ± 0.0005	3.5042 ± 0.0301
SUERC-13047	T45	0.0897 ± 0.0008	3.5810 ± 0.0449
SUERC-13048	T46	0.0815 ± 0.0007	3.4534 ± 0.0454
SUERC-13054	T48	0.0921 ± 0.0006	3.7059 ± 0.0442

Table 20: Final results for PP-4 quartz

The weighted mean of the PP-4 results presented in Table 20 is (3.5442 ± 0.056   x 10^5 atoms g^{-1} SiO_2 (n=5)) is not significantly different from the weighted mean value for PP-4 (3.5687 ± 0.051 x 10^{5} ^{14}C atoms g^{-1} SiO_2 (n=10) from the study of Miller *et al*. (2006). This would appear to indicate that the system is generating realistic results as the volume of CO_2 and the number of ^{14}C atoms matches those from other studies (Miller *et al*., 2006 and Lifton *et al.,* 2001).

3.2.4. Shielded quartz results

Naysmith *et al*. (2004) presented results for ^{14}C extracted from 5g of quartz which had >5 m of shielding by rock with a density of ~2.7 g cm^{-3}. This material should, in principle, be free from ^{14}C generated by cosmogenic neutron spallation reactions and therefore can be used as a first attempt in assessing the full system contamination based on a total quartz procedural blank for the extraction procedure. The results indicate that this quartz contained a measurable ^{14}C concentration, well above the lowest system blank level (by a factor of 10), suggesting that the ^{14}C could be coming from muon production.   It was decided for this study to obtain a

shielded quartz sample from greater depth therefore, a sample from a depth of 250 m below ground level was obtained. This should ensure that the sample has no measurable ^{14}C activity either from spallation or muon production. The results presented in Table 21 are for the shielded quartz sample used in this study and are presented in ^{14}C atoms g^{-1} SiO$_2$. The results for the shielded sample have had the average system blank subtracted from them prior to the final calculation of ^{14}C atoms present. As can be seen from Table 21, the number of ^{14}C atoms is very small (0.13-0.63 x 10^5 atoms g^{-1} SiO$_2$) proving that the sample has been well shielded from cosmogenic reactions that would have added ^{14}C activity to the sample.

SUERC No.	Sample Code	F ± 1σ	^{14}C Atoms (g^{-1} SiO$_2$ x 10^5)
SUERC-13055	T49	0.0382 ± 0.0006	0.6338 ± 0.0341
SUERC-13056	T50	0.0288 ± 0.0006	0.1313 ± 0.0327

Table 21: Shielded quartz sample collected from a depth of 250 m

When starting new processes in radiocarbon dating it is important to determine a procedural blank which can be used for the whole process. The number of ^{14}C atoms for this study has been calculated using system blanks as described in Chapter 2 and by Lifton *et al*., 2001. The problem with using system blanks as a procedural blank is that the pre-treatment stage in the process is not assessed. If you use a shielded quartz sample which is pre-treated, using routine laboratory pre-treatment methods, and then run it on the vacuum system, this sample will have gone through all the processes and is therefore suitable as a procedural blank for the whole process. In Table 22 the PP-4 samples have been recalculated using the shielded quartz sample as a procedural blank. The average value is 3.4306 ± 0.045 x 10^5 atoms g^{-1} SiO$_2$ (n=5) compared to the value 3.5442 ± 0.056 x 10^5 atoms g^{-1} SiO$_2$ (n=5) calculated using a system blank and the published result of 3.5687 ± 0.051 x 10^5 ^{14}C atoms g^{-1} SiO$_2$ (n=10)

(Miller *et al*., 2006). The shielded quartz sample will pick up all the contamination which is collected by the system blank in the vacuum system but it will also pick up any contamination during the pre-treatment stage.

SUERC No.	Sample Code	$F \pm 1\sigma$	^{14}C Atoms $(g^{-1}SiO_2 x10^5)$
SUERC-9557	T39	0.0789 ± 0.0007	3.4766 ± 0.0424
SUERC-9561	T41	0.0793 ± 0.0005	3.5043 ± 0.0301
SUERC-13047	T45	0.0897 ± 0.0008	3.3916 ± 0.0449
SUERC-13048	T46	0.0815 ± 0.0007	3.2639 ± 0.0454
SUERC-13054	T48	0.0921 ± 0.0006	3.5168 ± 0.0442

Table 22: PP-4 sample using a shielded quartz as procedural blank

CHAPTER 4

CONCLUSIONS

The initial measurements and results from a NERC funded grant to design a new system for extraction of *in-situ* produced ^{14}C from quartz were presented at the 18th International Radiocarbon Conference in New Zealand (Naysmith *et al.*, 2004) with the main conclusions being:- 1) the shielded and surface quartz samples that were analysed generated larger volumes of CO_2 than Lifton *et al.* (2001) and, 2) the results for the surface quartz sample (PP-4) obtained from the University of Arizona, and used as an in-house standard, only generated half the expected number of ^{14}C atoms.

The main aim of this study was to look at the conclusions from Naysmith *et al.* (2004) and to make improvements to the process to ensure the generation of reliable ^{14}C results from quartz samples. Significant progress has been made in improving the method for extraction and measurement of *in situ* ^{14}C. The main improvements to the vacuum system were:-

1) Changes to the clean up procedure. These appear to have improved the quality of the $CO_2.$ Passing the gas through a combination of an n-pentane/liquid nitrogen trap (-130°C), a copper and silver trap heated to 610°C and an iso-pentane/liquid nitrogen trap (-150°C) ensures a good clean up of the CO_2 gas extracted from the quartz and reliable graphitisation yields.

2) Improvements made to the handling of: (a) the quartz sleeve, which is placed inside the furnace to protect the Mullite tube during combustion and (b) the second quartz sleeve, which is used to transfer the sample boat to the furnace.

3) Heating tape being placed at each end of the furnace to reduce CO_2 absorption onto the cold glass.

4) Installing large 'O' ring joints at each end of the furnace for easier access to the furnace.

5) Installing a new Mullite tube in the furnace.

All these changes to the system mean that the vacuum line now generates volumes of CO_2 (0.0555 to 0.111 ml), which are lower than the CO_2 volumes (0.1488 to 0.2537 ml) from Naysmith *et al.* (2004) and now similar to the volumes of CO_2 (0.0587 to 0.0829 ml) published by Lifton *et al.* (2001). One of the main changes made from Naysmith *et al.* (2004) was the procedure for calculating numbers of ^{14}C atoms for system blanks for the extraction system, to bring it into line with that used by Lifton *et al.* (2001). In Naysmith *et al.* (2004) the system blank used was a 1ml dead CO_2 sample combusted in the furnace and converted into graphite. The problem of using this method was that the sample volume was too large compared to the volume generated by a single quartz combustion and would not pick up all the contamination in the system. In this study the system blank is a sample that is put through all steps in the extraction procedure and the CO_2 collected, added to dead CO_2 (to give a total volume of 1 ml) and graphitised. The value of the system blank is (0.88 ± 0.09 x 10^6 ^{14}C atoms), however, there is some variability within the system blank for this system, and it is not as low as that produced by Lifton on his system in Arizona (0.15 ± 0.01 x 10^6 ^{14}C atoms). The weighted mean of the PP-4 results in this study (3.4906 ± 0.041 x 10^5 ^{14}C atoms g^{-1} SiO_2 (n=5)) is statistically indistinguishable from the weighted mean value for PP-4 from Miller *et al.* (2006) (3.5687 ± 0.051 x 10^5 ^{14}C atoms g^{-1} SiO_2 (n=10)) which would appear to prove that our system is generating the correct number of ^{14}C atoms from quartz samples.

In the previous study we analysed a shielded quartz sample from a depth of 5 m below ground level, and the results showed a higher than expected ^{14}C activity. It was decided for this study to obtain a shielded quartz sample from greater depth therefore, a sample from a depth of 250 m

below ground level was obtained. This should ensure that the sample has no measurable ^{14}C activity from either spallation or muon production. The results for this sample indicate that the number of ^{14}C atoms is very small (0.13-0.63 x 10^5 atoms g^{-1} SiO_2) proving that the sample has been well shielded from all reactions that would have added ^{14}C activity to the sample. The shielded quartz samples were also used as a system blank to calculate the PP-4 results. The average value obtained was 3.3022 ± 0.041 x 10^5 atoms g^{-1} SiO_2 (n=5) compared to the value 3.4906 ± 0.041 x 10^5 atoms g^{-1} SiO_2 (n=5) calculated using the system blank and the published result of 3.5687 ± 0.051 x 10^5 ^{14}C atoms g^{-1} SiO_2 (n=10) from Miller *et al*. (2006). Any radioanalytical procedure requires the analysis of "blank" samples for determination of background activities, therefore, it seems logical that the shielded quartz sample from depth should be used as the system blank for the whole *in situ* ^{14}C extraction procedure. This is in conflict with the procedure of Lifton *et al.* (2001) and of course, results in significantly lower numbers of ^{14}C atoms.

The other difficulty in making *in situ* ^{14}C measurements is the man-hours required to complete the analysis. During this study it took three complete working days to run a sample through all the stages of the process. It would be a major advantage if this could be cut to two days, as this would then allow two samples to be analysed per week. This is a major consideration when, for example, trying to analyse five unknown quartz samples, as you need in the region of a further 10 standards to make the measurements and this requires a large time commitment, (45 days to prepare a batch for the AMS) which has to be taken into account when assessing the viability and feasibility of undertaking the analysis.

The procedures and data generated during this study have resulted in the SUERC laboratory, in partnership with the Department of Geographical and Earth Sciences Glasgow University, being able to further research in

this area with the attainment of funding to secure a 3-year Ph.D. studentship.

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