## The carbon cycle over the last 1000 years inferred from inversion of ice core data

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## Contents

1	Intr	roduction	1
<b>2</b>	The	e carbon cycle	5
	2.1	Introduction	5
	2.2	The atmosphere	7
	2.3	The terrestrial biosphere	9
	2.4	The oceans	11
	2.5	<sup>13</sup> C	18
	2.6	$^{14}$ C	24
	2.7	Estimating CO <sub>2</sub> fluxes from concentration measurements	26
	2.8	$CO_2$ and $\delta^{13}C$ ice core records	28
	2.9	Forcing mechanisms	35
		2.9.1 Anthropogenic inputs	35
		2.9.2 Climate	39
		2.9.3 Other natural forcings	46
	2.10	Methods for inversion of ice core records	47
	2.11	Previous inversions of ice core records	49
	2.12	Concluding remarks	51
	ъ		
3	Rec	constructing atmospheric trace gas records from firm and ice core	<b>-</b> 0
	mea	Asurements	53 F9
	ა.1 იი		03 E4
	ა.∠ ი ი	Description of firm processes	54 57
	3.3		57
		3.3.1 Basic equations $\ldots$	6U 60
	0.4	3.3.2 Finite difference implementation	62 64
	3.4		64
		$3.4.1  \text{Ice cores} \dots \dots$	64 65
	~ <b>~</b>	3.4.2 Specification of ice properties	65 70
	3.5	Model calculations for DE08-2	70
		3.5.1 Firn air composition	70
		3.5.1       Firn air composition         3.5.2       Gravitational fractionation         5.2       A	70 73
	9.6	3.5.1Firn air composition3.5.2Gravitational fractionation3.5.3Age distributions and effective ageDifference	70 73 76
	3.6	3.5.1       Firn air composition         3.5.2       Gravitational fractionation         3.5.3       Age distributions and effective age         Diffusion correction for isotopic ratios         2.6.1	70 73 76 82
	3.6	3.5.1       Firn air composition         3.5.2       Gravitational fractionation         3.5.3       Age distributions and effective age         Diffusion correction for isotopic ratios	70 73 76 82 84
	3.6	3.5.1Firn air composition	70 73 76 82 84 87

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	88
3.8       Firn $\delta^{13}$ CO <sub>2</sub> records       1         3.9       Concluding remarks       1         4       Calculations with a box diffusion carbon cycle model       1         4.1       Introduction       1         4.2       The box diffusion model       1         4.2       The box diffusion model       1         4.2       The box diffusion model       1         4.2.1       Model description       1         4.2.2       Model parameters and input data       1         4.3.5       Forward calculations       1         4.3.1 <sup>14</sup> C production from <sup>10</sup> Be data       1         4.3.2       Little lce Age calculations       1         4.3.3       Summer temperature anomaly record       1         4.4       Single deconvolution calculation       1         4.4.1       Calculated net fluxes       1         4.4.2       Bomb <sup>14</sup> C       1       1         4.4.3 $\delta^{13}C$ 1       1         4.5       Concluding remarks       1       1         5.1       Introduction       1       1         5.2.1       The Kalman filter       1       1         5.2.2       Smoothing <th>.00</th>	.00
3.9       Concluding remarks       1         4       Calculations with a box diffusion carbon cycle model       1         4.1       Introduction       1         4.2       The box diffusion model       1         4.2       The box diffusion model       1         4.2.1       Model description       1         4.2.2       Model parameters and input data       1         4.3       Forward calculations       1         4.3.1 <sup>14</sup> C production from <sup>10</sup> Be data       1         4.3.2       Little Ice Age calculations       1         4.3.3       Summer temperature anomaly record       1         4.4.3       Summer temperature anomaly record       1         4.4.3       Summer temperature anomaly record       1         4.4.1       Calculated net fluxes       1         4.4.2       Bomb <sup>14</sup> C       1       1         4.4.3 $\delta^{13}$ C       1       1         4.5       Concluding remarks       1       1         5       Kalman filter double deconvolution method       1       1         5.1       Introduction       1       5.2.3       Extended Kalman filter       1         5.2.3       Extended Kalman fi	.06
4       Calculations with a box diffusion carbon cycle model       1         4.1       Introduction       1         4.2       The box diffusion model       1         4.2.1       Model description       1         4.2.2       Model parameters and input data       1         4.3       Forward calculations       1         4.3.1       14 C production from <sup>10</sup> Be data       1         4.3.2       Little Ice Age calculations       1         4.3.3       Summer temperature anomaly record       1         4.4       Single deconvolution calculation       1         4.4.1       Calculated net fluxes       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.3 $\delta^{13}C$ 1         4.4.3 $\delta^{13}C$ 1         4.5       Concluding remarks       1         5.2       Methods       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosin	.14
4       Calculations with a box diffusion carbon cycle model       1         4.1       Introduction       1         4.2       The box diffusion model       1         4.2       Model description       1         4.2.1       Model description       1         4.2.2       Model description       1         4.2.2       Model description       1         4.3.1       Little lee Age calculations       1         4.3.2       Little lee Age calculation       1         4.3.3       Summer temperature anomaly record       1         4.4.3       Single deconvolution calculation       1         4.4.4       Single deconvolution calculation       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.3 $\delta^{13}$ C       1         4.5       Concluding remarks       1         5.6       Concluding remarks       1         5.1       Introduction       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing <td< th=""><th></th></td<>	
4.1       Introduction       1         4.2       The box diffusion model       1         4.2.1       Model description       1         4.2.2       Model parameters and input data       1         4.3       Forward calculations       1         4.3.1 <sup>14</sup> C production from <sup>10</sup> Be data       1         4.3.2       Little Ice Age calculations       1         4.3.3       Summer temperature anomaly record       1         4.4       Single deconvolution calculation       1         4.4.1       Calculated net fluxes       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.3< 6 <sup>13</sup> C       1       1         4.4.5       Concluding remarks       1         4.5       Concluding remarks       1         5.6       Methods       1         5.2.1       Introduction       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.2.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6       CO <sub>2</sub> and $\delta^{13}$ C: atmospheric pulse response	19
4.2       The box diffusion model       1         4.2.1       Model description       1         4.2.2       Model parameters and input data       1         4.3       Forward calculations       1         4.3       Forward calculations       1         4.3.1 <sup>14</sup> C production from <sup>10</sup> Be data       1         4.3.2       Little Ice Age calculations       1         4.3.3       Summer temperature anomaly record       1         4.4.3       Single deconvolution calculation       1         4.4.1       Calculated net fluxes       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.3 $\delta^{13}$ C       1         4.4.4       Single deconvolution method       1         4.4.5       Concluding remarks       1         4.4.3 $\delta^{13}$ C       1         4.5       Concluding remarks       1         5.2       Smothing       1         5.2.1       The Kalman filter       1         5.2.2       Smothing       1         5.2.3       Extended Kalman filter       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results	.19
4.2.1       Model parameters and input data       1         4.2.2       Model parameters and input data       1         4.3       Forward calculations       1         4.3.1 <sup>14</sup> C production from <sup>10</sup> Be data       1         4.3.2       Little Ice Age calculations       1         4.3.3       Summer temperature anomaly record       1         4.4.3       Single deconvolution calculation       1         4.4.1       Calculated net fluxes       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.3 $\delta^{13}$ C       1         4.5       Concluding remarks       1         4.4.3 $\delta^{13}$ C       1         4.5       Concluding remarks       1         5       Kalman filter double deconvolution method       1         5.1       Introduction       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6.1       Model formulation       1         5.6.2       Q based on	.20
4.2.2       Model parameters and input data       1         4.3       Forward calculations       1         4.3.1 $^{14}$ C production from $^{10}$ Be data       1         4.3.2       Little Ice Age calculations       1         4.3.3       Summer temperature anomaly record       1         4.4       Single deconvolution calculation       1         4.4.1       Calculated net fluxes       1         4.4.2       Bomb $^{14}$ C       1         4.4.3 $\delta^{13}$ C       1         4.4.4       Goncluding remarks       1         4.5       Concluding remarks       1         5       Kalman filter double deconvolution method       1         5.1       Introduction       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.2.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       So	.20
4.3       Forward calculations       1         4.3.1 <sup>14</sup> C production from <sup>10</sup> Be data       1         4.3.2       Little Ice Age calculations       1         4.3.3       Summer temperature anomaly record       1         4.3.3       Summer temperature anomaly record       1         4.4       Single deconvolution calculation       1         4.4.1       Calculated net fluxes       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.3 $\delta^{13}$ C       1         4.4.4       Bomb <sup>14</sup> C       1         4.4.5       Concluding remarks       1         4.5       Concluding remarks       1         5       Kalman filter double deconvolution method       1         5.1       Introduction       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.2.4       Choosing Q for ice core analysis       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6.1       Model formulation       1         5.6.2       Q	.23
4.3.1 <sup>14</sup> C production from <sup>10</sup> Be data       1         4.3.2       Little Ice Age calculations       1         4.3.3       Summer temperature anomaly record       1         4.3.3       Summer temperature anomaly record       1         4.4.3       Single deconvolution calculation       1         4.4       Single deconvolution calculation       1         4.4.1       Calculated net fluxes       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.3 $\delta^{13}$ C       1         4.5       Concluding remarks       1         5       Kalman filter double deconvolution method       1         5.1       Introduction       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1	.25
4.3.2       Little Ice Age calculations       1         4.3.3       Summer temperature anomaly record       1         4.4.3       Single deconvolution calculation       1         4.4.4       Single deconvolution calculation       1         4.4.1       Calculated net fluxes       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.3 $\delta^{13}$ C       1         4.5       Concluding remarks       1         5       Kalman filter double deconvolution method       1         5.1       Introduction       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       Source uncertainties       1         5.7.1       Model formulation       1         5.7.2       Results       1         5.7.3       Statistics       1	.28
4.3.3       Summer temperature anomaly record       1         4.4       Single deconvolution calculation       1         4.4.1       Calculated net fluxes       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.2       Bomb <sup>14</sup> C       1         4.4.3 $\delta^{13}$ C       1         4.5       Concluding remarks       1         5       Kalman filter double deconvolution method       1         5.1       Introduction       1         5.2       Methods       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1	.32
4.4       Single deconvolution calculation       1         4.4.1       Calculated net fluxes       1         4.4.2       Bomb       1 <sup>4</sup> C         4.4.3 $\delta^{13}$ C       1         4.4.3 $\delta^{13}$ C       1         4.4.3 $\delta^{13}$ C       1         4.4.3 $\delta^{13}$ C       1         4.5       Concluding remarks       1         5       Kalman filter double deconvolution method       1         5.1       Introduction       1         5.2       Methods       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       Source uncertainties       1	.34
4.4.1       Calculated net fluxes       1         4.4.2       Bomb $^{14}$ C       1         4.4.3 $\delta^{13}$ C       1         4.5       Concluding remarks       1         5       Kalman filter double deconvolution method       1         5.1       Introduction       1         5.2       Methods       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6       CO2 and $\delta^{13}$ C: atmospheric pulse response functions       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       Source uncertainties       1         5.7.1       Model formulation       1         5.7.2       Results       1         5.7.3       Statistics       1         5.7.4       Source uncertainties	.35
4.4.2       Bomb ${}^{14}C$ 1         4.4.3 $\delta^{13}C$ 1         4.5       Concluding remarks       1         5       Kalman filter double deconvolution method       1         5.1       Introduction       1         5.2       Methods       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6       CO <sub>2</sub> and $\delta^{13}$ C: atmospheric pulse response functions       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       Source uncertainties       1         5.7.1       Model formulation       1         5.7.2       Results       1         5.7.3       Statistics       1         5.7.4       Source uncertainties       1	.37
4.4.3 $\delta^{13}$ C       1         4.5       Concluding remarks       1         5       Kalman filter double deconvolution method       1         5.1       Introduction       1         5.2       Methods       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6       CO2 and $\delta^{13}$ C: atmospheric pulse response functions       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       Source uncertainties       1         5.7.1       Model formulation       1         5.7.2       Results       1         5.7.3       Statistics       1         5.7.4       Source uncertainties       1	.39
4.5       Concluding remarks       1         5       Kalman filter double deconvolution method       1         5.1       Introduction       1         5.2       Methods       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6       CO2 and $\delta^{13}$ C: atmospheric pulse response functions       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       Source uncertainties       1         5.7.1       Model formulation       1         5.7.2       Results       1         5.7.3       Statistics       1         5.7.4       Source uncertainties       1	.40
5	.45
5       Kaiman inter double deconvolution method       1         5.1       Introduction       1         5.2       Methods       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6       CO <sub>2</sub> and $\delta^{13}$ C: atmospheric pulse response functions       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       Source uncertainties       1         5.7.1       Model formulation       1         5.7.2       Results       1         5.7.3       Statistics       1         5.7.4       Source uncertainties       1	4 17
5.1       Introduction       1         5.2       Methods       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing $\mathbf{Q}$ for ice core analysis       1         5.5       Discussion of methane results       1         5.6       CO <sub>2</sub> and $\delta^{13}$ C: atmospheric pulse response functions       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       Source uncertainties       1         5.7.1       Model formulation       1         5.7.2       Results       1         5.7.3       Statistics       1         5.7.4       Source uncertainties       1	41
5.2       Methods       1         5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6       CO <sub>2</sub> and $\delta^{13}$ C: atmospheric pulse response functions       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       Source uncertainties       1         5.7.1       Model formulation       1         5.7.2       Results       1         5.7.3       Statistics       1         5.7.4       Source uncertainties       1	.41
5.2.1       The Kalman filter       1         5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6       CO <sub>2</sub> and $\delta^{13}$ C: atmospheric pulse response functions       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       Source uncertainties       1         5.7       CO <sub>2</sub> and $\delta^{13}$ C: mixed layer pulse response functions       1         5.7.1       Model formulation       1         5.7.2       Results       1         5.7.3       Statistics       1         5.7.4       Source uncertainties       1	.40
5.2.2       Smoothing       1         5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6       CO <sub>2</sub> and $\delta^{13}$ C: atmospheric pulse response functions       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       Source uncertainties       1         5.7       CO <sub>2</sub> and $\delta^{13}$ C: mixed layer pulse response functions       1         5.7.1       Model formulation       1         5.7.2       Results       1         5.7.3       Statistics       1         5.7.4       Source uncertainties       1	.48
5.2.3       Extended Kalman filter       1         5.3       Previous applications of Kalman filtering to trace gas studies       1         5.4       Choosing Q for ice core analysis       1         5.5       Discussion of methane results       1         5.6       CO <sub>2</sub> and $\delta^{13}$ C: atmospheric pulse response functions       1         5.6.1       Model formulation       1         5.6.2       Q based on firn smoothing       1         5.6.3       Results       1         5.6.4       Source uncertainties       1         5.7       CO <sub>2</sub> and $\delta^{13}$ C: mixed layer pulse response functions       1         5.7.1       Model formulation       1         5.7.2       Results       1         5.7.3       Statistics       1         5.7.4       Source uncertainties       1	.92 EC
5.3Previous applications of Kalman filtering to trace gas studies5.4Choosing Q for ice core analysis5.5Discussion of methane results5.6 $CO_2$ and $\delta^{13}C$ : atmospheric pulse response functions5.6.1Model formulation5.6.2Q based on firn smoothing5.6.3Results5.6.4Source uncertainties5.7 $CO_2$ and $\delta^{13}C$ : mixed layer pulse response functions5.7.1Model formulation5.7.2Results5.7.3Statistics5.7.4Source uncertainties	.00
5.4 Choosing <b>Q</b> for ice core analysis $\dots \dots \dots$	.08
5.5Discussion of methane results15.6 $\operatorname{CO}_2$ and $\delta^{13}$ C: atmospheric pulse response functions15.6.1Model formulation15.6.2 $\mathbf{Q}$ based on firn smoothing15.6.3Results15.6.4Source uncertainties15.7 $\operatorname{CO}_2$ and $\delta^{13}$ C: mixed layer pulse response functions15.7.1Model formulation15.7.2Results15.7.3Statistics15.7.4Source uncertainties1	.00
5.6 $\operatorname{CO}_2$ and $\delta^{13}$ C: atmospheric pulse response functions	.00
5.6.1Model formulation15.6.2Q based on firn smoothing15.6.3Results15.6.4Source uncertainties15.7 $CO_2$ and $\delta^{13}C$ : mixed layer pulse response functions15.7.1Model formulation15.7.2Results15.7.3Statistics15.7.4Source uncertainties1	.69
5.6.2 Q based on firn smoothing $\dots \dots \dots$	.69
5.6.3Results15.6.4Source uncertainties15.7 $CO_2$ and $\delta^{13}C$ : mixed layer pulse response functions15.7.1Model formulation15.7.2Results15.7.3Statistics15.7.4Source uncertainties1	72
5.6.4 Source uncertainties $\dots \dots \dots$	.74
5.7 $CO_2$ and $\delta^{10}C$ : mixed layer pulse response functions $\dots \dots \dots$	.76
5.7.1       Model formulation       1         5.7.2       Results       1         5.7.3       Statistics       1         5.7.4       Source uncertainties       1	.81
5.7.2       Results	.81
5.7.3 Statistics	87
5.7.4 Source uncertainties	.90
	.95
5.8 Comparison between the Kalman filter double deconvolution and the mass	
	.98
5.9 Concluding remarks	:01
6 Investigating the carbon cycle	05
6.1 Isofluxes	205
6.2 Discussion of double deconvolution results	215
6.3 Natural variability	

		6.3.1 Century time scale
		$5.3.2$ Decadal time scale $\ldots \ldots 223$
	6.4	The 1940s flattening
		6.4.1 Actual and reconstructed variations
		6.4.2 Fluxes
		6.4.3 Climate
	6.5	Anthropogenic trend
	6.6	Concluding remarks
7	Sun	mary and Further Work 241
	7.1	Summary
	7.2	Further work $\ldots \ldots 244$
	Refe	ences

## Abstract

A new record of  $CO_2$  and  $\delta^{13}CO_2$  over the last 1000 years from air trapped in Antarctic ice is analysed. The ice core record, from Law Dome in Antarctica, has high time resolution and high precision, and overlaps the modern  $CO_2$  record. A model of diffusion and bubble trapping in firm is developed and used to interpret the ice core measurements in terms of past atmospheric changes. The firm model quantifies the smoothing effects of diffusion and bubble trapping on atmospheric signals. A method for correcting firm and ice core  $\delta^{13}C$  measurements for the fractionating effects of the firm diffusion process on different isotopes is developed and applied. The Law Dome ice core record is compared with other firm  $\delta^{13}C$  records.

A 1-D global carbon cycle model is used to interpret variations in CO<sub>2</sub> and  $\delta^{13}$ C in terms of natural and anthropogenic sources and sinks. A major feature in the ice core record is the decrease in CO<sub>2</sub>, and increase in  $\delta^{13}$ C, through the 'Little Ice Age' period (roughly 1550–1800). Model calculations indicate that the observed decrease in CO<sub>2</sub> is consistent with either terrestrial or oceanic exchange, however the increase in  $\delta^{13}$ C favours a terrestrial response to cooling and argues against an oceanic sink.

A new double deconvolution method using the Kalman filter is developed and applied to the Law Dome record. The method incorporates statistics into the carbon cycle modelling, and allows more detailed analysis of CO<sub>2</sub>,  $\delta^{13}$ C and flux variability. It removes the need to fit smoothing splines to the ice core measurements prior to interpretation. A particular advantage of the method is that uncertainties on the deduced fluxes are estimated as part of the calculation.

The double deconvolution calculation suggests that natural variability in  $CO_2$  fluxes may be as large as 1 GtC y<sup>-1</sup> on the time scale of just less than a decade. The Law Dome  $CO_2$  measurements show a slight decrease in  $CO_2$  around the 1940s. The firn and carbon cycle models suggest that about 3 GtC y<sup>-1</sup> uptake (mostly oceanic) is required in the 1940s to match the ice core measurements. The estimates of variation in the terrestrial biospheric flux between 1950 and 1980 from the double deconvolution calculation are in very good agreement with estimates of the global terrestrial flux from a climate-driven ecosystem model of Dai and Fung (1993). A detailed comparison of estimates of the isotopic disequilibrium flux (isoflux) for <sup>13</sup>C is given. This is to certify that this thesis contains no material that has been accepted for the award of any other degree or diploma in any university or other institution and that, to the best of my knowledge, it contains no material previously published or written by another person, except where due reference is made in the thesis.

Catherine Trudinger

Publications arising from and associated with this work:-

Trudinger, C.M., I.G. Enting, D.M. Etheridge, R.J. Francey, V.A. Levchenko, L.P. Steele,
D. Raynaud and L. Arnaud, Modeling diffusion and bubble trapping in firm. J. Geophys. Res., 102D, p 6747-6763, 1997.

Trudinger, C.M., I.G. Enting, R.J. Francey, D.M. Etheridge and P.J. Rayner, Long-term variability in the global carbon cycle inferred from a high-precision CO<sub>2</sub> and  $\delta^{13}$ C ice-core record. *Tellus*, 51B, p 233-248, 1999.

Levchenko, V.A., D.M. Etheridge, R.J. Francey, C. Trudinger, C. Tuniz, E.M. Lawson, A.M. Smith, G.E. Jacobson, Q. Hua, M.A.C. Hotchkis, D. Fink, V. Morgan and J. Head. Measurements of the <sup>14</sup>CO<sub>2</sub> bomb pulse in firn and ice at Law Dome, Antarctica, *Nucl. Instr. and Meth. Phys. Res. B.*, *123*, p 290-295, 1997.

Francey, R.J., C.E. Allison, D.M. Etheridge, C.M. Trudinger, I.G. Enting, M. Leuenberger, R.L. Langenfelds, E. Michel and L.P. Steele, A 1000-year high precision record of  $\delta^{13}$ C in atmospheric CO<sub>2</sub>. *Tellus*, 51B, p 170-193, 1999.

Rayner, P.J., R. Giering, T. Kaminski, R. Ménard, R. Todling and C.M. Trudinger, Exercises, in *Inverse Methods in Global Biogeochemical Cycles*, edited by P. Kasibhatla, M. Heimann, P. Rayner, N. Mahowald, R. Prinn and D. Hartley, American Geophysical Union Monograph 114, p 81-106, 2000.

For my father, Wal Trudinger in loving memory

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Figure 1: Law Dome  $CO_2$  ice core record (grey dots) and selected events from the second millennium AD