

atmosphere is  $\sim 4^{\circ}\text{C}$ . This result suggests that the warming caused by the doubling of  $\text{CO}_2$ -content would be  $\sim 2^{\circ}\text{C}$ . This is significantly less than the warming which is estimated by the general circulation model of Manabe and Wetherald<sup>10</sup> with idealised geography and without seasonal variation of insolation. Table 1 also reveals that the area mean warming of the Northern Hemisphere is significantly larger than that of the Southern Hemisphere. This interhemispheric difference results partly from the smallness of the snow albedo-feedback effect over the Antarctic ice sheet where surface albedo differs little between the  $1 \times \text{CO}_2$  and  $4 \times \text{CO}_2$ -experiments.

In view of the assumption of fixed cloudiness and various simplifications contained in the sea ice modelling, the quantitative aspect of the present results should be received with caution. However, this study suggests that the warming of the atmosphere in response to an increase in  $\text{CO}_2$ -content of the air will have significant seasonal and interhemispheric asymmetries.

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## Carbon disulphide and carbonyl sulphide from biogenic sources and their contributions to the global sulphur cycle

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Estimates of the magnitude of biogenic sulphur emissions range from  $\sim 70\%$  of the total atmospheric sulphur burden<sup>1–7</sup>, and the chemical nature of the emissions has not been clearly established. Conway<sup>1</sup> speculated that the principal volatile biogenic component of the sulphur cycle was hydrogen sulphide ( $\text{H}_2\text{S}$ ) whereas Lovelock *et al.*<sup>8</sup> and Rasmussen<sup>9</sup> have suggested that dimethyl sulphide (DMS) contributes to the apparent source deficits. Aneja *et al.*<sup>10</sup> have shown that both  $\text{H}_2\text{S}$  and DMS are emitted from saltmarshes. Other volatile sulphur compounds which may contribute to the sulphur burden of the atmosphere include methyl mercaptan ( $\text{CH}_3\text{SH}$ )<sup>11,12</sup>, dimethyl disulphide ( $(\text{CH}_3)_2\text{S}_2$ )<sup>11,12</sup>, carbonyl sulphide ( $\text{COS}$ )<sup>13</sup> and carbon disulphide ( $\text{CS}_2$ )<sup>14,15</sup>. We report here the discovery of  $\text{CS}_2$  and  $\text{COS}$  emanating from a saltmarsh and estimate their emission rates using emission flux reactor and bag chamber techniques. The species  $\text{CS}_2$  and  $\text{COS}$  are relatively inert in the troposphere, so may be assumed to penetrate to the stratosphere, where they may be photolysed to form the sulphur dioxide ( $\text{SO}_2$ ) and sulphates ( $\text{SO}_4^{2-}$ ) known to be present in the stratosphere. Based on the measured fluxes, we show that the emissions from marshes are important to the sulphate aerosol burden ( $\leq 19\%$ ) of the stratosphere, but not important for the tropospheric sulphur burden ( $\leq 0.2\%$ ).

An emission flux reactor (chamber) was used for measuring Earth-atmosphere fluxes of biogenic sulphur compounds. The chamber technique has high sensitivity for flux measurement without the necessity of measuring very low concentrations. In addition, gas residence times in the emission flux reactor are of the order of minutes so that chemical transformations between emission and analysis may be minimised. The chamber used by Aneja<sup>11</sup> and Hill *et al.*<sup>12</sup> was modified by making the walls from 5-mil ( $\sim 0.13$  mm) thick FEP Teflon supported by an exterior aluminium frame. This design was chosen to provide negligible attenuation of ambient light.

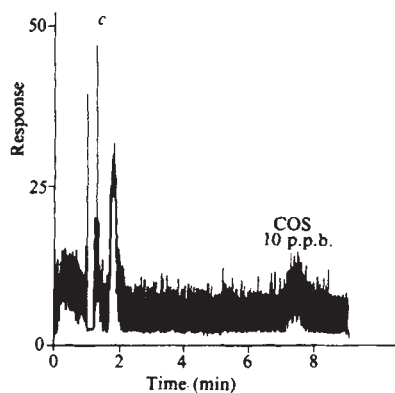
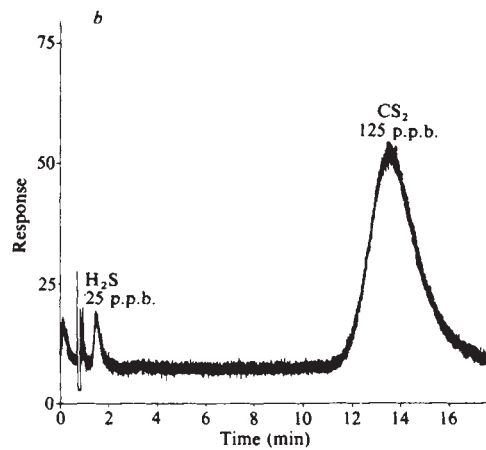
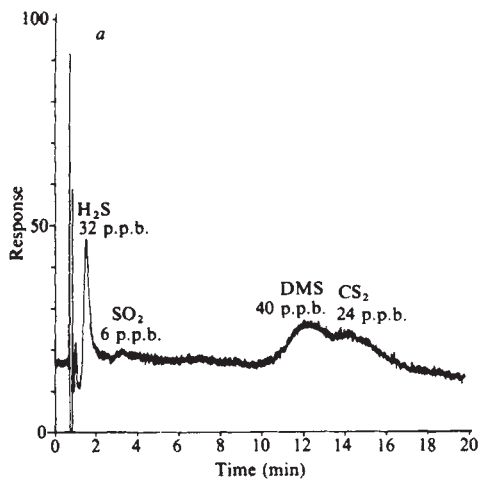
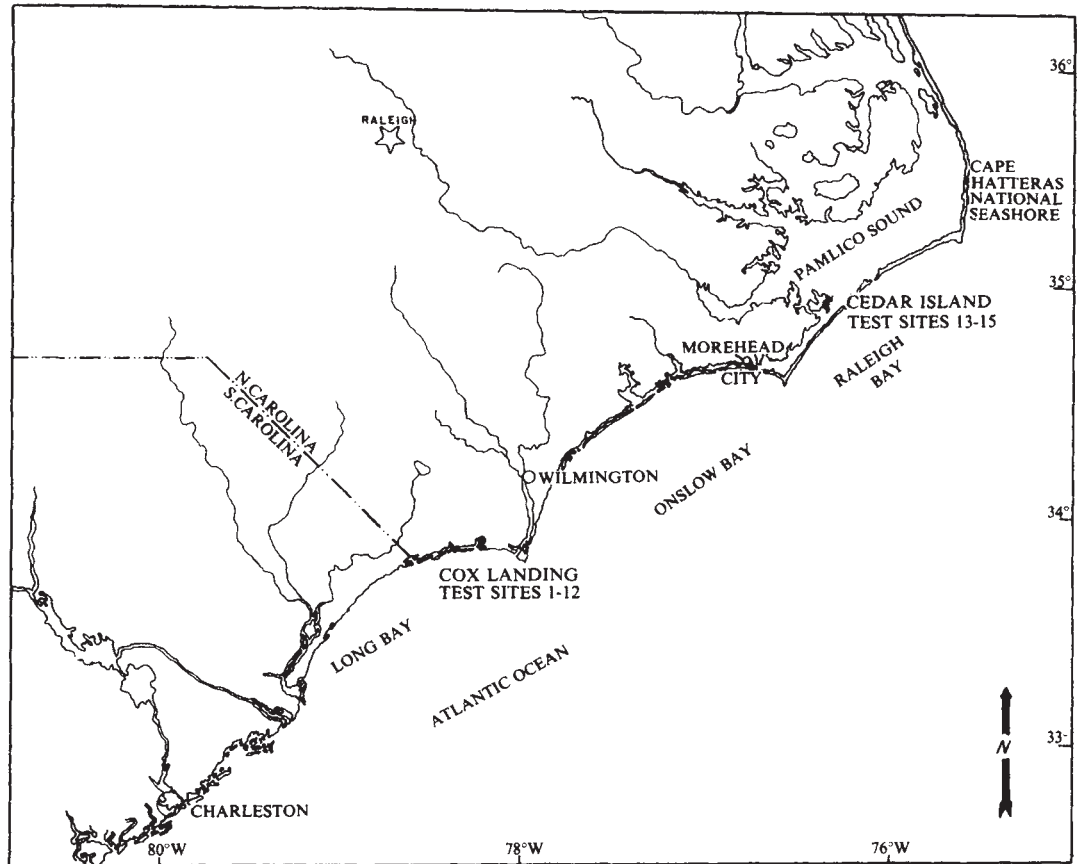
The analytical instrument used was a gas chromatograph (Tracor 270HA) equipped with a flame photometric detector. A 394-nm interference filter made the detector sensitive to sulphur compounds. A 36-foot ( $\sim 11$  m) FEP Teflon column ( $\frac{1}{8}$  inch (0.32 cm) o.d.) packed with 40–60 mesh Teflon coated with 5% polyphenyl ether (PPE) and 0.5% phosphoric acid was used at  $50^{\circ}\text{C}$  to separate gaseous sulphur species<sup>17</sup>. The carrier gas was nitrogen with a flow rate of  $\sim 81$  ml  $\text{min}^{-1}$ . The retention time for  $\text{CS}_2$  in these conditions is  $\sim 14$  min which allows a good separation from  $\text{H}_2\text{S} + \text{COS}$  (1.5 min),  $\text{SO}_2$  (3.1 min), and  $\text{CH}_3\text{SH}$  (5.0 min). The overlapping DMS (12.2 min) and  $\text{CS}_2$  peaks were manually resolved into separate contributions. This column did not resolve  $\text{H}_2\text{S}$  and  $\text{COS}$ , so these species were separated by incorporating a second 19-foot (5.8 m) FEP Teflon column ( $\frac{1}{8}$  inch (0.32 cm) o.d.) packed with 50/80 mesh Porapak QS in parallel with the first. The two columns were incorporated in the flow lines separately by a pneumatically controlled switching system. The carrier gas for the second column was nitrogen with a flow rate of  $\sim 40$  ml  $\text{min}^{-1}$ . The retention time for  $\text{COS}$  in these conditions is  $\sim 8$  min, which allows a good separation from  $\text{H}_2\text{S}$  (retention time  $\sim 5.5$  min); however, this column retained  $\text{CS}_2$ . The gas chromatograph was calibrated for both columns in the laboratory and in the field using a dilution system and bag samples.

Intensive measurements were made for biogenic sulphur species at Cox's Landing, Long Beach, North Carolina; and at Cedar Island Wildlife Refuge, North Carolina, which are saltmarshes on the east coast of the US (Fig. 1). Experiments were performed during late summer at both locations. At Cox's Landing, 12 different test sites were selected. At each test site, two identical emission flux reactors were placed next to each other. One was flushed with pure gaseous nitrogen (de-aerated) and the other with ambient air (aerated). This was done to gain information on the oxygen-depleted gaseous environment, as well as to maintain the integrity of the emitted sulphur compounds in the de-aerated case. Sampling was done over mud flats, over regions close to marsh grass where the vegetation was decaying, and over marsh grass (*Spartina alterniflora*) clipped to about 1 inch above ground level. Time-integrated bag samples of the effluent gas from the emission flux reactor were collected every 30 min. These bag samples were analysed within 30 min for various gaseous sulphur species in a controlled environment mobile laboratory parked at the edge of the marsh. All the experiments at Cox's landing were performed to study the emission fluxes of  $\text{CS}_2$  for diurnal and tidal variations. During the experiments, the ambient temperature ranged between  $19.1$  and  $33.4^{\circ}\text{C}$ , sediment temperature with the tide out ranged from  $24.2$  to  $32.6^{\circ}\text{C}$ , and the water temperature with the tide in was between  $23.8$  and  $31.2^{\circ}\text{C}$ .

Figure 2a is a typical chromatogram (using the PPE column) of sulphur gases emitted from the saltmarsh. It indicates the presence and identity of  $\text{CS}_2$  and various other biogenic sulphur species.

The average emission rates of  $\text{CS}_2$  at the various types of test sites are given in Table 1. In 20 of the 172 aerated runs,  $\text{CS}_2$  was detected; and  $\text{CS}_2$  appeared only one in the de-aerated case. All of the data in Table 1 are for the aerated case. The  $\text{CS}_2$  emission rates in the mud flat zone in the presence and absence of a water column for varying light conditions were less than  $0.05$  g  $\text{m}^{-2}$   $\text{yr}^{-1}$  (this is the emission rate based on the lowest detectable  $\text{CS}_2$  concentration).  $\text{CS}_2$  is also evolved over and in

**Fig. 1 a**, Location of the sites. Sites 1-12 were at Cox's Landing and Sites 13-15 at Cedar Island.



**Fig. 2 a**, Chromatogram of volatile sulphur compounds from *Spartina* zone. The chromatogram was obtained at Cox's Landing using the PPE column and a nonlinear sulphur-specific flame photometric detector (FPD). **b**, Chromatogram of volatile sulphur compounds obtained from enclosed *Spartina* stem. The chromatogram was obtained at Cox's Landing using the PPE column and a nonlinear sulphur-specific FPD. **c**, Chromatogram of volatile sulphur compounds resolved on a Porapak QS column. The sample was obtained at Cedar Island.

**Table 1** Emission rate measurements of CS<sub>2</sub>

Test site characteristic	Mean emission rate of all runs, gS m <sup>-2</sup> yr <sup>-1</sup> (no. of runs)	Mean of runs with emission rate greater than detectable limit*‡, gS m <sup>-2</sup> yr <sup>-1</sup> (no. of runs)
Over mud flat zone (direct emission rate measurement*) August 1977	<0.05 (100)	— (0)
Over decaying <i>Spartina</i> zone (direct emission rate measurement*) August 1977	~0.04 (61)	0.19 ± 0.07 (13)
Over <i>Spartina alterniflora</i> zone (direct emission rate measurement*) August 1977	0.13 (11)	0.21 ± 0.06 (7)
Enclosed single <i>Spartina alterniflora</i> plant (indirect emission rate measurement†) July 1978	0.20 (10)	0.20 ± 0.09 (10)

\* Direct emission rate  $n = (F \cdot \Delta C / A)$ , where  $F$  = steady volumetric flow rate of gas through the chamber;  $\Delta C$  = concentration increase;  $A$  = area of emitting surface covered by the chamber. Based on the CS<sub>2</sub> detectable limit of the instrument, the corresponding emission rate is <0.05 gS m<sup>-2</sup> yr<sup>-1</sup>, and the CS<sub>2</sub> analytical error is ±3% of the estimated value.

† Indirect emission rate  $n = (S \cdot \Delta C \cdot V) / t \times 8,760$ , where  $S$  = no. of stems per m<sup>2</sup>;  $\Delta C$  = concentration increase, parts per 10<sup>9</sup>;  $V$  = volume of chamber (1.96 × 10<sup>-3</sup> m<sup>3</sup>);  $t$  = time of enclosure (h). For this measurement, the CS<sub>2</sub> detectable limit is 0.017 gS m<sup>-2</sup> yr<sup>-1</sup> and the CS<sub>2</sub> analytical error is ±3% of the estimated value.

‡ Values are given ±s.d.

the vicinity of *Spartina alterniflora* under the aerated emission flux reactor in the presence and absence of a water column and the fluxes range from <0.05 to ~0.3 gS m<sup>-2</sup> yr<sup>-1</sup> (Table 1). CS<sub>2</sub> may be formed at a juncture of the carbon and sulphur cycles by either biogenic or chemical activity. These observations show that CS<sub>2</sub> is certainly produced in an aerated environment, and that it may be formed in a de-aerated environment. Lovelock<sup>15</sup> has observed that CS<sub>2</sub> can originate in anaerobic conditions on the sea floor, while, in the *Spartina alterniflora* zone, we observe it more often in aerobic conditions. The reasons for the differences between the aerated and de-aerated chamber runs are not yet known.

These observations suggest that *Spartina alterniflora* plants may be associated with the production of CS<sub>2</sub>. This association is also supported by the results of an indirect method of estimating gaseous sulphur flux (see ref. 18 for the enclosure method). A single stem was enclosed for ~6 h in a Pyrex glass cylindrical chamber of ~1.96 litre volume (~100 cm long and ~5 cm i.d.). Samples were collected during day and night. Ten such experiments were performed and *in situ* syringe samples (one for each stem) were withdrawn from the glass chambers and analysed on the gas chromatograph. In all cases large quantities of CS<sub>2</sub> were observed (see Fig. 2b and Table 1).

Seneca *et al.*<sup>19</sup> have determined the stem density in North Carolina coastal saltmarshes to be ~200 ± 25 stems m<sup>-2</sup>. Based on this result, the emission rate of CS<sub>2</sub> from *Spartina alterniflora* stems is estimated to be ~0.2 gS m<sup>-2</sup> yr<sup>-1</sup> (Table 1). Note that this indirect emission rate measurement leads to emission rate values similar to those obtained by direct flux measurement over the *Spartina* zone (Table 1).

At Cedar Island three different test sites were selected over *Spartina alterniflora* and mud flat zones. At each test site the emission flux reactor was used in the aerated mode only. All the experiments described (Table 2) were performed to study the emission fluxes of COS. It establishes the presence and identity of COS as indicated by the gas chromatogram in Fig. 2c. The indirect method of estimating gaseous sulphur flux revealed no release of COS from *Spartina alterniflora* plants.

To estimate the per cent of biogenic contribution of CS<sub>2</sub> and COS to the global tropospheric sulphur cycle, we assumed that all marshes are completely made up of *Spartina alterniflora* and that they emit uniformly. We took the total marsh area<sup>20</sup> as 3.8 × 10<sup>5</sup> km<sup>2</sup>, and assumed that 100 × 10<sup>6</sup> tons of gaseous sulphur are emitted per year from the biosphere by natural processes<sup>4</sup>. Based on our CS<sub>2</sub> indirect and COS direct emission rates (~0.2 gS m<sup>-2</sup> yr<sup>-1</sup> and 0.03 gS m<sup>-2</sup> yr<sup>-1</sup>, respectively) and the above assumptions, the contribution of CS<sub>2</sub> and COS from marshes is a small portion, <0.07% and 0.09%, respectively, of the biogenic sulphur. Obviously, more work is needed to characterise the global processes adequately.

We also estimated the contributions of CS<sub>2</sub> and COS emissions to the stratospheric sulphate aerosol layer. According to Crutzen's<sup>16</sup> estimate, a flux of ~1.8 × 10<sup>-4</sup> gS m<sup>-2</sup> yr<sup>-1</sup> into the stratosphere will account for the entire stratospheric sulphate aerosol layer. Applying Junge's<sup>21</sup> one-dimensional eddy diffusion model to the troposphere, and using the present CS<sub>2</sub> and COS average emission rate for global marshes and CS<sub>2</sub> and COS atmospheric lifetimes<sup>14</sup> of 1 yr and 20 yr respectively, an upper limit to the contributions can be made by assuming zero CS<sub>2</sub> and COS concentrations at 15 km height (average Junge aerosol layer ~20 km). The upper limit contributions are 8% for CS<sub>2</sub> and 11% for COS. However, if land plants emit CS<sub>2</sub> at rates comparable to those measured for *Spartina alterniflora* the biogenic emissions of CS<sub>2</sub> could account for the entire Junge layer. Experiments are under way to test for CS<sub>2</sub> emissions for land vegetation.

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**Table 2** Emission rate measurements of COS

Test site characteristic	Mean emission rate of all runs, gS m <sup>-2</sup> yr <sup>-1</sup> (no. of runs)	Mean of runs with emission rate greater than detectable limit‡, gS m <sup>-2</sup> yr <sup>-1</sup> (no. of runs)
Over mud flat zone (direct emission rate measurement*) July 1978	0.05 (2)	0.05 ± 0.01 (2)
Over decaying <i>Spartina</i> zone (direct emission rate measurement*) July 1978	0.01 (2)	0.02 (1)
Over <i>Spartina alterniflora</i> zone (direct emission rate measurement*) July 1978	0.03 (7)	0.04 ± 0.03 (6)
Enclosed single <i>Spartina alterniflora</i> plant (indirect emission rate measurement†) July 1978	<0.01* (10)	<0.01* (0)

\* Based on the COS detectable limit of the instrument, the corresponding emission rate is <0.01 gS m<sup>-2</sup> yr<sup>-1</sup> and the COS analytical error is ±20% of the estimated value. See Table 1.

† See Table 1.

‡ Values given ±s.d.

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## Tidal flexure of ice shelves measured by tiltmeter

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A new design of tiltmeter has been used to measure the tidal bending of the Ronne Ice Shelf, Antarctica. By this means the point at which the ice sheet leaves the land and starts floating on the sea has been defined to within 600 m. Monitoring this position in future should give an indication of the state of balance of the West Antarctic ice sheet, often considered<sup>1</sup> to be unstable even if not actually disintegrating. The hydrostatic level meter is light and simple and can operate unattended while recording continuously for periods of several weeks. Observations at eight different sites on Rutford Ice Stream (Fig. 1) gave tidal records on ice more than 1,700 m thick and at points up to 600 km from the nearest open sea.

Antarctic ice shelves are floating ice sheets varying in thickness from 100 m to more than 1,700 m. They rise and fall on the ocean tide, bending over a narrow region where they join the grounded ice sheet. The variation in theoretical surface elevation profiles over the duration of a tidal cycle have been derived<sup>1,2</sup> for several constitutive laws, but there have been no published measurements of tidal changes in profiles. The reason is partly because there are crevasse fields in many hinge zones and partly because of the lack of a suitable measurement technique. Gravimeters, strain meters and optical methods all have serious drawbacks because of their cost or their logistic and manpower requirements. The hydrostatic level meter, however, is a stable, continuously recording and relatively cheap instrument that, once placed in a shallow trench in the snow surface to reduce temperature and atmospheric effects, can operate

unattended for long periods. For a short base length (5 m in our case) the instrument will measure changes in surface gradient which can be integrated along a transect to obtain a surface profile.

There are several reasons for wanting to measure tidal flexing. Actual profiles can be compared with theoretical<sup>1,2</sup> profiles in order to deduce the most appropriate constitutive law. There is evidence that the crystal orientation fabric of the ice can be significantly altered as it passes across the hinge zone<sup>3</sup>. A knowledge of strain rates is necessary for calculating the development of the fabric<sup>4</sup> and its effect on the flow law. Plastic deformation of ice in the bending zone dissipates tidal energy<sup>5</sup>, but for a precise estimate both the constitutive law and the region over which bending occurs must be known. By measuring tidal constants it will be possible to study the interaction of tide not only with the main body of an ice shelf<sup>6</sup> but also with its grounding region. The stability of ice sheets grounded below sea level is thought to be controlled by the shielding effect of ice shelves<sup>7</sup>; tidal flexing may effect the dynamic behaviour in the hinge zone and may thus be an important consideration in the possible disintegration of the West Antarctic ice sheet<sup>8</sup>. By locating accurately the position of the grounding line any future changes can easily be monitored.

An instrument was required which would measure tilts of the ice surface as small as  $10^{-6}$  radians with as large a dynamic range as possible. Tiltmeters currently available were considered unsuitable mainly because of the difficulty of mounting them on ice; all were intended to be installed in boreholes to give the necessary stability. In most materials and particularly in ice, such a hole takes several days to become mechanically and dimensionally stable. We therefore decided to use an instrument which could measure the height difference between two separated points on the glacier surface. The hydrostatic level meter consists of two vessels containing a liquid connected by a tube so that the liquid surface forms a gravitational potential (Fig. 2); a second tube connects the air space above the liquid at each end. Instruments of this form have been used for many purposes, for example for precision levelling on Hawaii<sup>9</sup> but the liquid height has been read by direct optical means and attempts to make an automatically recording instrument using floats with displacement transducers, ultra-sonic measurement of fluid level, or mercury capacitance transducers have only been a success in laboratory conditions.

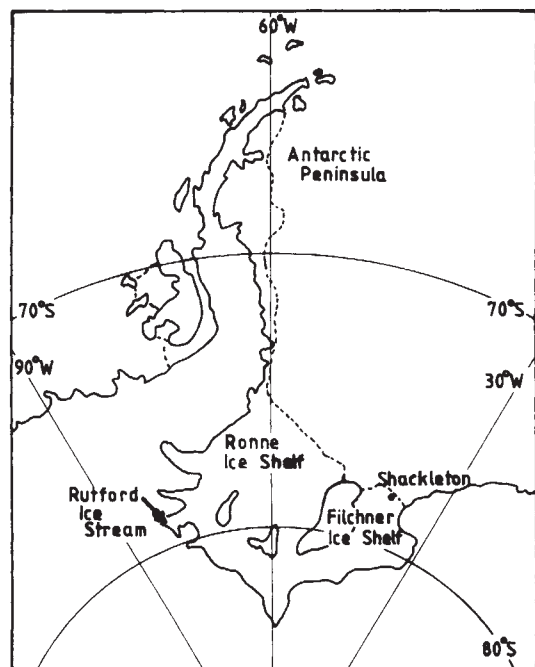


Fig. 1 Map showing location of tiltmeter sites.