matters arising

Variation with time of a Sun–weather effect

THE reported[1] influence of the solar and interplanetary magnetic sector structure on terrestrial atmospheric vorticity at the 500-mbar level during the winters of 1963–73 has been disputed by Williams and Gerety[2]. We consider, however, that the response has been remarkably constant if an apparent decrease during the past few years of the intensity of tropospheric circulation is properly accounted for.

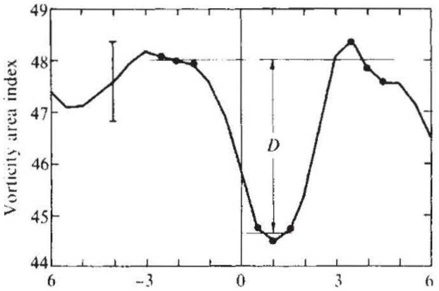

Fig. 1 A superimposed epoch analysis of the vorticity area index at 500 mbar about 162 times of interplanetary magnetic sector boundary transits during the winters in the interval 1 November 1963 to 31 March 1976 for which spacecraft observations of boundary transits are available. A typical error bar (twice the s.e.m.) is shown for the point at day −4.

First, Hines and Halevy[3] concluded that "If solar sector boundary crossings are to be employed in the determination of key dates, their times of occurence must be identified to at least an accuracy of ±24 h on average for the analysis to be successful. This constraint is not serious when spacecraft data are employed for the determination of field reversals, but it can become significant when indirect determinations are made from ground-based geomagnetic measurements"[4,5].

Second, Hines and Halevy[3] introduced the excursion x, defined as the difference between the maximum and minimum values of the vorticity area index (VAI) found in a 12-d interval centred on the time of boundary transit. The amplitude of the Sun–weather influence was small when the excursion was small and large when the excursion was large. In the past few years the observed excursions have been considerably smaller than in the previous years.

The interval during which spacecraft observations of the interplanetary magnetic field are available is the winter months from 1 November 1963 to 31 March 1976. The response of the VAI at 500 mbar to 162 sector boundary transits past the Earth during this spacecraft interval is shown in Fig. 1. The previously reported[1] minimum in VAI approximately one day after boundary transit is clear. A measure D of the depth of this minimum is defined as the average VAI near days −2 and +4 (w.r.t. day 0 as the boundary transit time) minus the average VAI near day 1. For each specified day the average VAI during three adjacent half-days is computed. In Fig. 1, $D = 3.30 \times 10^5$ km^2.

D is found[3] to increase as x increases; x_s divides the 162 boundary transits during the spacecraft interval into two equal groups, one with larger excursions and one with smaller. The Sun–weather effect is examined separately for each group.

Consider now the three-winter interval from 1 November 1963 to 31 March 1966. Figure 2 shows, for this interval (plotted at 1965), the average value of D associated with the group of boundary transits having excursions $>x_s$, and the average D for the group of boundary transits having excursions $<x_s$. The analysis is repeated one year at a time between 1 November 1975 and 31 March 1978 (plotted at 1977), the last for which data are available.

Between 1963 and the present shown in Fig. 2, the size of the Sun–weather associated with the group of boundaries having larger excursions is rather constant. For each interval shown in Fig. 2, D is larger for the group of boundaries associated with larger excursions than for the group of boundaries associated with smaller excursions, thus confirming in a much larger data set the result of Hines and Halevy[3]. Except for the winters 1968–71, D associated with the group of boundary transits having smaller excursions is close to zero.

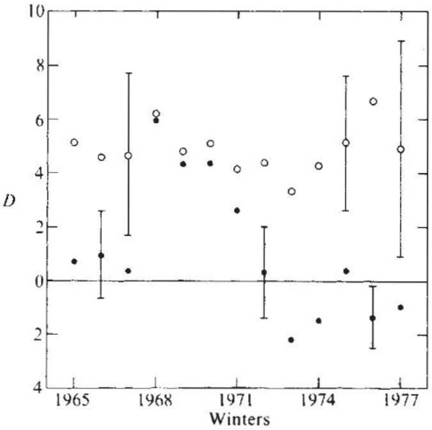

Fig. 2 D for the groups of boundary transits having larger excursions (○) and for the groups of boundary transits having smaller excursions (●). The results for the last winters should be considered preliminary until spacecraft observations of boundary transits are available. The total length of the error bar is twice the s.e.m.

During the winters of the spacecraft interval shown in Fig. 3 the number of boundary transits whose excursions were $>x_s$ and the number of boundary transits with excursions $<x_s$ are approximately equal (note x_s was defined to make them equal during the entire spacecraft interval). In recent winters the magnitude of the excursions has declined considerably such that in the last interval only seven boundary transits had excursions $>x_s$ while 31 transits did not. If this decline is not an artefact of the meteorological data processing, an important change in the large-scale tropospheric circulation in the Northern Hemisphere has occurred in the past few years.

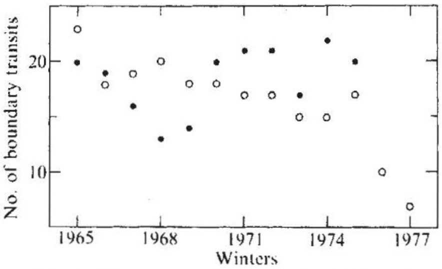

Fig. 3 The number of boundary transits in each three-winter interval for which the excursions are in the larger group (○) and in the smaller group (●). Note that in the last two intervals the number of boundary transits with larger excursions is considerably decreased.

In the winters before the spacecraft interval only indirect determinations of boundary transits made from ground-based geomagnetic measurements are available. Using these indirect boundary transits no consistent Sun–weather effect similar to that shown in Fig. 2 is found. It is quite possible that there was a variation in the Sun–weather effect in these earlier years, but the situation is complicated by the lack of spacecraft observations.

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WILLIAMS REPLIES—The biggest weakness of the study by Wilcox and Scherrer is immediately apparent. In subdividing the keydates according to their excursion, Wilcox and Scherrer have allowed themselves freedom to select the data *a posteriori*. Despite the work of Hines and Halevy[1] there is no known physical reason for selecting the data in this manner. In this context, it must be remembered that the data has already been carefully selected, for example the wintertime, 500 or 300 mbar VAI is chosen since it exhibits the best result. Unfortunately, in the absence of a physical understanding this is one of the few ways in which we can progress. Indeed, I have been working along similar lines[2].

A lesser weakness has been pointed out by Hines and Halevy[1]. If one hypothesises that the 'signal' is the remnant of the 'noise' in the VAI dataset, then one might also expect the signal to increase as the noise increases. However, one would not expect the consistency claimed by Wilcox and Scherrer. A new point along these lines concerns the definition of the excursion. If the signal is real, then the strength of the signal can hardly depend on the meteorological noise after day 0 since then one would merely be correlating the signal with itself. Therefore, I would like to see the analysis repeated, this time selecting keydates according to the excursion before the start of the signal.

With regard to more minor points, I would like to see the results of the same analysis at 300 mbar; and how sensitive is Fig. 3 to a small change in x_s?

If the signal is real and does depend on the intrinsic variability of the atmosphere, then this is an important result which ought to have strong implications for the search for a mechanism. In this case the study of Wilcox and Scherrer should be taken further to answer some important questions. For example is there a critical excursion below which no effect occurs? Is there a proportionality between the excursion and the amplitude of the signal? (The winters 1968–71, which could be interpreted as 1967–71 in view of the 3-y average employed and the '1967' and '1972' results, seem to suggest this is not so.) Can the winter–summer asymmetry of the result be explained in this manner, since one could expect the excursion to be less in summer?

The simplest interpretation of the VAI–SSB effect still seems to be statistical chance. This belief has been reinforced by an interpretation of this effect in terms of the tropospheric energetics in the wavenumber domain[3].

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Anionic copolymerisation of episulphides with elemental sulphur

PENCZEK *et al.*[1] believe that the anionic copolymerisation of propylene sulphide (PS) with elemental sulphur gives the high-molecular weight polysulphide polymers $-\mathrm{CH_2{-}CH(CH_3){-}S}_x-$ (% S up to 90%, that is, $x = 12$). Nevertheless, PS mainly yields copolymers with $x \leqslant 2$ (refs 2, 3). We believe that this contradiction[1-3] is caused by the presence of residual sulphur in the PS copolymers[1], which can be detected in the elementary analysis and does not show up in the NMR spectra. This assumption is based on our experimental data[2] and also confirmed by ^{13}C NMR data[1] which indicate that PS copolymers with $x \leqslant 2$, and not polysulphide polymers with x up to 12 (ref. 1), are being formed. Indeed, polypropylene sulphide ($x = 1$) is characterised by the signals δ20.7 for CH$_3$, δ38.6 for CH$_2$ and δ41.0 and 41.2 for CH[4], whereas polypropylene disulphide ($x = 2$)[5] is characterised by the signals δ19.05 for CH$_3$, δ44.6 and 45.0 for CH$_2$ and δ46.0 and 46.4 p.p.m. for CH[6]. The spectra of PS copolymers with $2 > x > 1$ also have the signals of conjunctive units $-\mathrm{SS{-}CH_2{-}CH(CH_3){-}S{-}CH_2{-}CH(CH_3){-}SS}-$ at δ39.9 and 39.5 for CH, δ37.4 for CH$_2$ and δ19.4 p.p.m. for CH$_3$ (ref. 6). Therefore the increase in the intensity of signals 45.8, 45.6, 39.5, 39.1 and 19.4 p.p.m. with the increasing sulphur content in PS copolymers[1] are due to the increase in the amount of disulphide bonds ($x = 2$), and not polysulphide bonds ($x > 2$) as other signals in the spectra are absent (for example, CH$_3$ signal of trisulphide units should appear at δ18.1 p.p.m.[6]). It follows that the apparent values of $x = 2$ and 5 in the spectra of PS copolymers[1] conform to $x \leqslant 1.5$ and 1.7, respectively. Like the ^{13}C NMR data[1,2], ^{1}H NMR spectra of PS copolymers[2] correspond to that of PS polymers with a varying ratio of mono- and disulphide units[6].

We have shown previously[2,3] that the probability of a polysulphide polymer formation increases as the nucleophilic reactivity of episulphides decreases. Very reactive ethylenesulphide is predominantly converted into polyethylene sulphide ($x = 1$). Polysulphide polymers ($x > 2$) are mainly produced from a less reactive cyclohexene sulphide, isobutylene sulphide and trimethylethylenesulphide. The latter forms the copolymers with x up to 7 whose ^{1}H NMR spectra show a gradual downfield shift of proton signals as x is increased in the case of more reactive PS. The probability of homopolymerisation and formation of stable disulphide units increases as unstable polysulphide chains must split at hard reaction conditions[1]. The stereochemical effect of substituents and more mild copolymerisation conditions[2] apparently decrease the homopolymerisation rate of substituted episulphides and thereby increase the probability of their copolymerisation with sulphur as well as stabilise and restrict the participation of polysulphide chains (at least for $x \leqslant 5$) in nucleophilic splitting reactions because of the sterically hindered growing thiolate anions. Thus, despite these limitations, which can be overcome by using active forms of sulphur, inorganic polysulphides or UV irradiation[2], this method offers broad possibilities in the synthesis of polysulphide polymers[2,3].

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PENCZEK *ET AL.* REPLY—Aliev *et al.* have confirmed a general principle of anionic copolymerisability of elemental sulphur[1], including copolymers with various cyclic sulphides as described in our patent[2]. However, Aliev *et al.* assume that copolymers of propylene sulphide with elemental sulphur could have merely be solid solutions of polysulphide polymers $-\mathrm{CH_2{-}CH(CH_3){-}S}_x-$ with an average $\bar{x} < 2$ and elemental sulphur. This was based on their failure to prepare in their system copolymers of propylene sulphide with higher sulphur content, and on their interpretation of the ^{13}C-NMR spectra. However, great care must be taken with the interpretation of the NMR spectra of polysulphides, because we observed recently that the upfield signals can be caused by the presence of the low-molecular weight cyclic polysulphides. These products were removed from our polymers by an extensive extraction with boiling methyl alcohol (unreacted sulphur was removed in the same way)[3].

Had Aliev *et al.* attempted to repeat our experiments, leading to the true copolymers with high content of the built in sulphur, it would have become clear that, for example, a 50:50 mixture of polypropylene sulphide and elemental

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