*EXPRESS LETTER*

# Helium in old porcelain: The historical variation of the He isotopic composition in air

JUN-ICHI MATSUDA,[1]* TAKUYA MATSUMOTO[1,2] and AKIHISA SUZUKI[1]

[1]Department of Earth and Space Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan
[2]Institute for Study of the Earth's Interior, Okayama University, 827 Yamada, Misasa, Tottori 682-0193, Japan

It is still debated whether there is a variation of the atmospheric $^3$He/$^4$He ratio, due to the anthropogenic release of radiogenic $^4$He contained in fossil fuels, in modern era. In this study, we measured the He isotopic ratios in old Chinese and Japanese porcelains assuming that the old atmosphere might have been preserved in vesicles. The trapped noble gases are elementally but not isotopically fractionated. The $^3$He/$^4$He ratios in some old Chinese porcelain are significantly higher than the present air value, indicating that recent human industrial activity might have affected the helium isotopic ratio of the atmosphere. Our result indicates that the rate of change in the atmospheric $^3$He/$^4$He ratio was $-0.034 \pm 0.018$ %/year ($2\sigma$) in the last 200 years. Results show that porcelain can be used as a time capsule of the paleoatmosphere during historical age.

## INTRODUCTION

Helium is the second abundant element in the universe. It has two isotopes: $^3$He and $^4$He. The accepted $^3$He/$^4$He ratio in the present atmosphere is $1.39 \times 10^{-6}$ that is an averaged value of $(1.399 \pm 0.013) \times 10^{-6}$, measured in Leningrad, USSR (St-Petersburg, Russia) in 1970 (Mamyrin *et al.*, 1970) and $(1.384 \pm 0.006) \times 10^{-6}$, measured in Ontario, Canada in 1976 (Clarke *et al.*, 1976). Helium abundance in the atmosphere is constant and it results from the flux balance between the degassing from the solid Earth and the escape to space. The mixing time of helium in the atmosphere is less than 10 years, much shorter than its residence time of $10^6$ years. Thus the helium isotopic ratios in air is expected to be constant at least for $10^3$ years as far as helium degassing from the Earth is at the steady-state on this timescale. However, since the Industrial Revolution, human industrial activities have released much radiogenic $^4$He into the atmosphere from consuming coal and petroleum. Thus it is likely that anthropogenic activity has changed the helium isotopic ratio in air as it has increased the $CO_2$ concentration in the atmosphere in the last 200 years. Oliver *et al.* (1984) reported the volume fraction of helium in the

atmosphere in 1981 as $5.222 \pm 0.017$ ppm, that is identical with the accepted value of $5.239 \pm 0.004$ ppm determined by Glueckauf (1946) within the uncertainties. Oliver *et al.* (1984) estimated that ~3 to $12 \times 10^{16}$ cm$^3$STP of $^4$He were released into the atmosphere by natural gas production between 1939 and 1981. According to them, ~50% of the total gas production was concentrated between 1971 and 1981. Thus the release of $^4$He should be higher than the above estimated value by a factor of three or four in 2010. Helium isotopic ratio is more sensitive than the He content to these anthropogenic changes because the released crustal helium has the isotopic ratio ($3$–$7 \times 10^{-8}$) lower than that of air by about two orders of magnitude.

Sano *et al.* (1989) indicated that there is a historical variation of the He isotopic ratio in the atmosphere from measurements of twenty air samples between 1977 and 1988 (18 from Japan and 2 from USA). They reported that the $^3$He/$^4$He ratio in air decreased at a rate of $-(1.06 \pm 0.76) \times 10^{-9}$/year (about 0.08%) during this period. However, Lupton and Graham (1991) questioned it and they suggested a changing rate of $+0.0093 \pm 0.043\%$ using four air samples between 1973 and 1990 (California, USA). Their obtained rate is not different from zero within the error, indicating that there is no significant historical variation of the atmospheric helium isotopic ratio. Lupton and Evans (2004) further reported that the decreasing rate is consistent with zero value using Pacific marine air sam-

*Corresponding author (e-mail: matsuda@ess.sci.osaka-u.ac.jp)

*Table 1. Concentrations and isotopic ratios of He and Ar in porcelain*

| Sample (g) | Location age | [⁴He] (10⁻⁸ cm³STP) | ³He/⁴He (Ra) | [³⁶Ar] (10⁻⁸ cm³STP) | ³⁸Ar/³⁶Ar | ⁴⁰Ar/³⁶Ar | Gas extraction method |
|---|---|---|---|---|---|---|---|
| POR1 | Japan | 2.1 | 0.935 ± 0.080 | 6.2 | 0.1875 ± 0.0005 | 300.2 ± 3.3 | Crushing (1000 strokes) |
| (1.65 g) | 2002AD | | | | | | |
| POR1-2 | | 4.9 | 0.972 ± 0.049 | 6.8 | 0.1880 ± 0.0005 | 299.1 ± 3.3 | Crushing (1000 strokes) |
| (1.36 g) | | | | | | | |
| POR2 | China | 86 | 1.072 ± 0.029 | | | | Crushing* |
| (17.9 g) | 1400AD | | | | | | |
| | | 82 | 1.147 ± 0.050 | | | | 2nd Crushing* |
| POR2-2 | | 6.4 | 1.071 ± 0.071 | | | | Fusion (1600°C) |
| (0.796 g) | | | | | | | |
| POR5 | China | 10 | 0.910 ± 0.040 | 27 | 0.1883 ± 0.0018 | 297.9 ± 2.9 | Crushing (1000 strokes) |
| (3.98 g) | 1550AD | | | | | | |
| POR6 | China | 2.0 | 0.676 ± 0.070 | 7.7 | 0.1882 ± 0.0017 | 292.7 ± 2.7 | Crushing (1000 strokes) |
| (2.98 g) | 1600AD | | | | | | |
| POR7 | Japan | 11 | 0.889 ± 0.048 | 18 | 0.1884 ± 0.0010 | 296.3 ± 2.5 | Crushing (30 strokes) |
| (3.27 g) | 1750AD | | | | | | |
| | | 4.2 | 0.952 ± 0.082 | 7.9 | | | 2nd Crushing (300 strokes) |
| POR8 | Japan | 19 | 0.976 ± 0.036 | | | | Crushing (300 strokes) |
| (4.51 g) | 1750AD | | | | | | |
| POR9 | China | 6.6 | 1.071 ± 0.048 | | | | Fusion (1600°C) |
| (0.635 g) | 1700AD | | | | | | |
| POR9-2 | | 0.68 | 1.017 ± 0.026 | 23 | 0.1876 ± 0.0004 | 295.5 ± 2.4 | Fusion (1600°C) |
| (0.785 g) | | | | | | | |
| POR9-3 | | 9.8 | 1.047 ± 0.044 | 36 | | | Crushing (300 strokes) |
| (2.53 g) | | | | | | | |
| POR10 | China | 3.7 | 1.052 ± 0.056 | 25 | 0.1874 ± 0.0009 | 293.1 ± 2.4 | Crushing (300 strokes) |
| (4.10 g) | 1700AD | | | | | | |
| Present air | | | 1 | | 0.188 | 295.5 | |

*For this sample, we used the large crusher where a piston allows gentle crushing of the sample by turning a handle (Matsuda et al., 1996). For other samples, we used the crusher using a piston moving up and down with an external compressed air (Matsumoto et al., 2001). So, the stroke numbers are given.*

ples between 1973 and 2003. Meanwhile, Pierson-Wickmann *et al.* (2001) analyzed the gas trapped in metallurgical slags from France and United Arab Emirates from 900 to 1991AD, and reported that the ³He/⁴He ratio in the sample of 1500AD was higher than that of the present air by 3.6 ± 1.2% (4.0 ± 3.5% for the 1900AD sample). Thus it is still debated whether helium isotopic ratio in air has decreased historically or not.

In this study, we aimed to investigate the historical variation of the He isotopic composition of the terrestrial air. We targeted Chinese and Japanese porcelains, because it is expected that they can preserve old atmosphere in confined vesicles formed during their production. The producing process of porcelain is as follows: (1) kneading of powders of clay minerals, talc, calcite etc. with water; (2) shaping in desired forms; and (3) sintering at about 1000°C. If the temperature of sintering is higher than the melting point of the raw material, the porcelain cannot preserve its shape. Thus the air, trapped as small

bubbles at kneading, should be preserved in vesicles in porcelain even after the sintering. Radiogenic helium (⁴He) in the raw material would be degassed at the sintering process and well mixed with a large amount of the ambient atmosphere, which we can also check from isotopic ratios in our measurements.

## SAMPLES AND EXPERIMENTS

We used seven porcelain samples from China and Japan produced at 1400AD (China), 1550AD (China), 1600AD (China), 1700AD (China), 1750AD (Japan) and 2002AD (Japan). The production age of the porcelain has been estimated from archaeological studies except for the 2002AD sample. The samples were crushed or fused at 1600°C in vacuum and the extracted gas was analyzed. The total gas amounts and isotopic ratios of helium (and of argon for some samples) were determined with a VG5400 noble gas mass spectrometer at Osaka Univer-
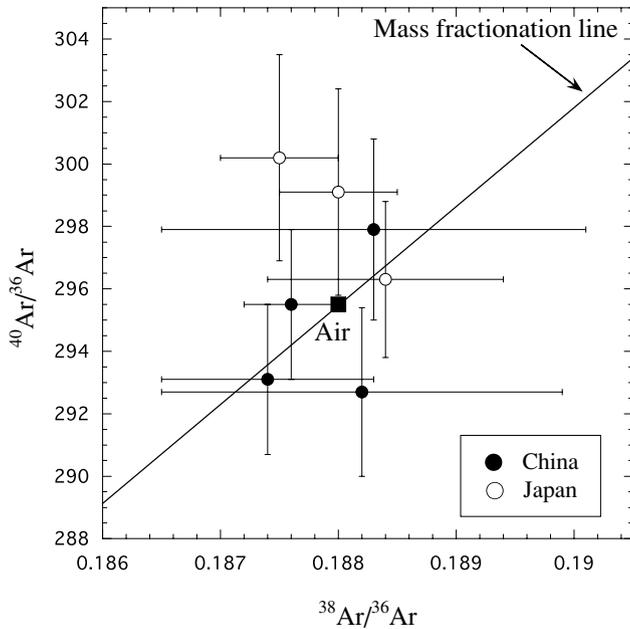
*Fig. 1. The $^{38}Ar/^{36}Ar$ vs. $^{40}Ar/^{36}Ar$ ratios diagram of old porcelain. Closed circles are Chinese porcelains and open circles are Japanese porcelains. All data cluster around the present-day atmospheric value.*

sity. The details of the crushing apparatus and the procedure of noble gas analyses are given elsewhere (Matsuda *et al*., 1996; Matsumoto *et al*., 2001). The hot blank amounts were $^4He = 1.0–1.4 \times 10^{-9}$ cm$^3$STP and $^{36}Ar = 0.2–1.3 \times 10^{-10}$ cm$^3$STP. He isotopic ratios measured in samples were calibrated against the artificial internal He Standard of Japan (HESJ; Matsuda *et al*., 2002) several times, showing a variation of ±1.7%.

## RESULTS AND DISCUSSION

The obtained results are given in Table 1. Quoted errors for isotopic ratios (1σ) include uncertainties associated with the ion counting at the measurement, blank corrections, isotope discrimination factors, etc. The errors of the gas amounts of $^4He$ and $^{36}Ar$ are about 5%. We simply listed the gas amount without normalizing it by the sample weight. The $^3He/^4He$ ratio is listed with the unit of "Ra" (1 Ra is the $^3He/^4He$ ratio of the present atmosphere). The He and Ar isotopic ratios are very similar to those of the present atmosphere (Table 1). Especially, gases extracted either by crushing or by heating yielded $^{40}Ar/^{36}Ar$ ratios isotopically identical to the present-day atmosphere (Fig. 1), suggesting that the sintering process completely removed the radiogenic component inherited from the raw material. In Fig. 1, the $^{40}Ar/^{36}Ar$ ratios of Japanese porcelain seem to be slightly higher than those in Chinese porcelain. This suggests that

the removal of the radiogenic component is not complete in Japanese porcelain, probably because their sintering temperature is lower than that of Chinese porcelain. Indeed, it is known that burning wood was used for the sintering of Japanese porcelain, but coal for Chinese porcelain.

The measured $^3He/^4He$ ratios have been plotted against the production year in Fig. 2. Here, we note that $^3He/^4He$ ratios of all the Japanese samples are similar to or slightly lower than the present air value and those of two Chinese samples of 1550AD and 1600AD show clearly lower $^3He/^4He$ ratios. These lower ratios are not surprising as they can be readily explained by the addition of radiogenic $^4He$ remaining in the raw material. However, three $^3He/^4He$ ratios measured by crushing and heating the 1400AD POR2 sample and four $^3He/^4He$ ratios from 1700AD samples exhibit slightly higher values than the present atmosphere. Data obtained at 1700AD are from two different samples (POR9 and POR10) both of which yielded consistently higher $^3He/^4He$ ratios by crushing and by heating. The average $^3He/^4He$ ratio for the three POR2 samples at 1400AD is 1.097 ± 0.031 Ra (1σ). The average value for the four data at 1700AD is 1.047 ± 0.022 Ra (1σ). Due to the uncertainties of these two averaged ratios, it would be premature to conclude that $^3He/^4He$ ratios had decreased in a time span of 300 years. Taking into account for the uncertainties of their production years, it would be safe to take an average (1.068 ± 0.018 Ra, 1σ) of both data sets as a representative of the pre-1700AD value for the $^3He/^4He$ ratio of atmosphere, i.e., before the Industrial Revolution.

Whether we treat the 1400AD and 1700AD data separately or not, some samples yield $^3He/^4He$ ratios significantly higher than the present-day ratio. This simple observation needs some explanation. One possibility is that the isotopic ratio was fractionated when He was trapped in the vesicles. However, Ar isotopic ratios indicate that the isotopic fractionation is negligible (less than 1%). Meanwhile, it should be noted that $^4He/^{36}Ar$ ratios are much higher than that of air in some samples (Table 1). Thus, we could suspect that trapped noble gases are elementally and isotopically fractionated and thus enriched in lighter isotopes, such as $^3He$. To examine it, we plotted the $^3He/^4He$ ratios against the $^4He/^{36}Ar$ ratio normalized to the air value (Fig. 3). If the high $^3He/^4He$ ratios were caused by mass fractionation, the data points should lie on the mass fractionation line, which is not the case (Fig. 3). Furthermore, samples with higher $^3He/^4He$ ratios have rather low $^4He/^{36}Ar$ ratios. Thus it is concluded that the trapped gas was elementally, but not isotopically fractionated.

So, we conclude that the measured $^3He/^4He$ ratios higher than the present-day air value represent the atmospheric He ratios when the porcelain was made. Our re-
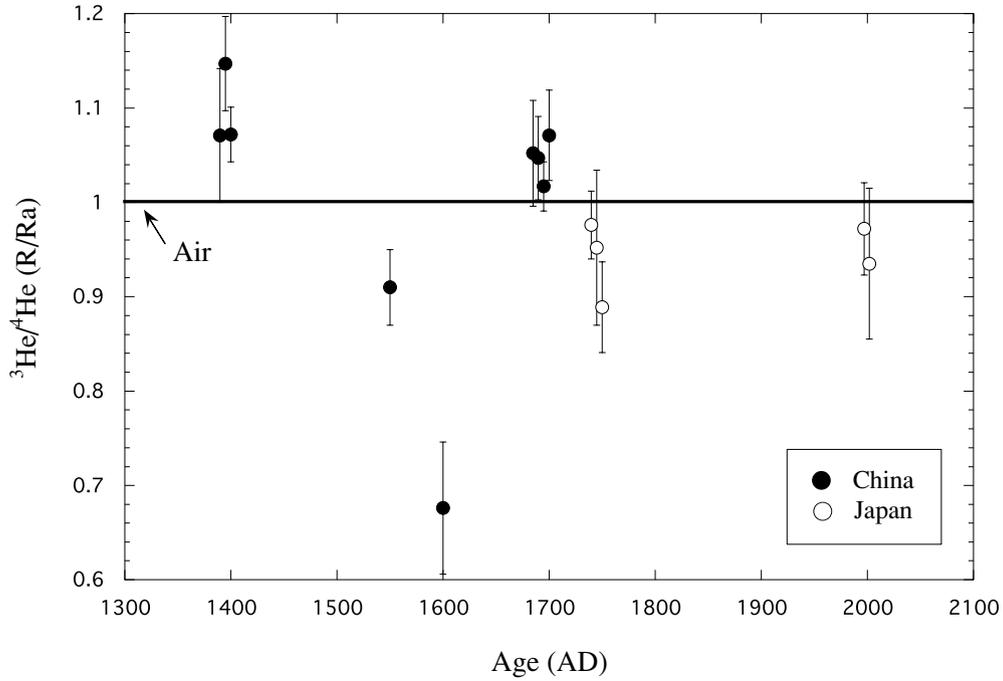
Fig. 2. The $^3$He/$^4$He ratio vs. production age of old porcelain. Symbols are the same as those in Fig. 1. Note that 1400AD and 1700AD samples have $^3$He/$^4$He ratios higher than that of the present-day atmosphere.



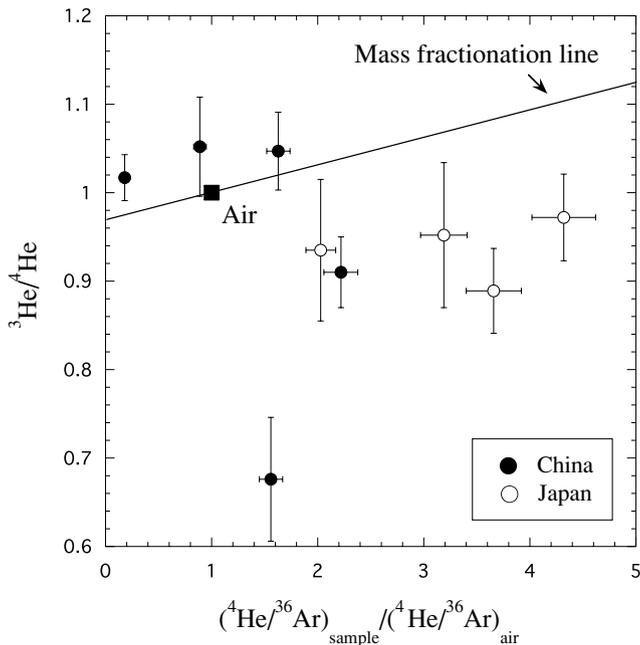Fig. 3. The $^3$He/$^4$He vs. ($^4$He/$^{36}$Ar)$_{sample}$/($^4$He/$^{36}$Ar)$_{air}$ ratios of old porcelain. Symbols are the same as those in Fig. 1. Note that data do not lie on the mass fractionation line.

sults indicate that the $^3$He/$^4$He ratio in air before the Industrial Revolution was higher than the present value by 6.8 ± 1.8% that is almost twice the value of 3.6 ± 1.2% (2$\sigma$) obtained from slags of 1500AD by Pierson-Wickmann et al. (2001). If we assume that $^3$He/$^4$He ratio decreased linearly during 200 years since the Industrial Revolution (middle 18 century) to 1970AD (the year measured by Mamyrin et al., 1970), the rate of change in the atmospheric $^3$He/$^4$He ratio would be –0.034 ± 0.009%/ year (1$\sigma$).

Table 2 compares the rate of change of the atmospheric $^3$He/$^4$He ratio (within 2$\sigma$ error) so far obtained by various authors. Our obtained value (–0.034 ± 0.018%/year) is barely compatible with +0.0093 ± 0.043%/year obtained by Lupton and Graham (1991) within the error. It seems difficult to detect –0.034%/year from recent air measurements on a short time span of 20 years. Lupton and Evans (2004) reported the change rate between –0.0102 and +0.0019%/year from the measurements of air samples collected over a 30-years interval. Using the He/C ratio and the fossil fuel consumption, Pierson-Wickmann et al. (2001) estimated the decreasing rate of the atmospheric $^3$He/$^4$He ratio as –0.014 ± 0.007%/year (Table 2). Our obtained value is larger than this estimation (Pierson-Wickmann et al., 2001). This difference can be explained by the large uncertainties existing on the anthropogenic $^4$He flux estimates. Lupton and Evans (2004) and Sano (1998) estimated the rate of change of the atmospheric

*Table 2. Comparison of the rate of change of $^3He/^4He$ ratio in air*

| Authors | Rate of change of $^3He/^4He$ ratio (%/year, $2\sigma$) | Samples |
|---|---|---|
| *From experiments* | | |
| Sano *et al.* (1989) | $-0.081 \pm 0.115$[a] | Air |
| | $-0.081 \pm 0.062$[b] | Air |
| Lupton and Graham (1991) | $+0.0093 \pm 0.043$ | Air |
| Pierson-Wickmann *et al.* (2001) | $-0.018 \pm 0.006$[c] | Slag |
| Lupton and Evans (2004) | $-0.0102$ to $+0.0019$ | Air |
| This work | $-0.034 \pm 0.018$[c] | Porcelain |
| | | |
| *From theoretical estimation* | | |
| Lupton and Evans (2004) | $-0.085 \pm 0.061$[d] | |
| Sano (1998) | $-0.033$ | |
| Pierson-Wickmann *et al.* (2001) | $-0.014 \pm 0.007$ | |

[a]*This value is suggested by the comment by Lupton and Graham (1991).*
[b]*This value is due to the reply by Sano et al. (1991).*
[c]*We assumed that the decrease of $^3He/^4He$ ratio is during recent 200 years since the Industrial Revolution.*
[d]*Estimation is based on the data of Oliver et al. (1984).*

$^3He/^4He$ ratio of $-0.085 \pm 0.061$%/year and $-0.033$%/year, respectively. Their rate of change is compatible with our obtained value of $-0.034 \pm 0.018$%/year, strongly supporting that the human activities since the Industrial Revolution modified the $^3He/^4He$ ratio of the atmosphere.

Finally, we would like to stress that manmade sintered material like porcelain might be considered as a new and reliable paleoenvironmental proxy to be used as a time capsule of the paleo-atmosphere in historical age.

## REFERENCES

Clarke, W. B., Jenkins, W. J. and Top, Z. (1976) Determination of Tritium by mass spectrometric measurement of $^3He$. *Int. J. App. Radiat. Isot.* **27**, 515–522.

Glueckauf, E. (1946) A microanalysis of the helium and neon contents of air. *Proc. Roy. Soc. Ser. A* **185**, 98–119.

Lupton, J. E. and Evans, L. (2004) The atmospheric helium isotope ratio: Is it changing? *Geophys. Res. Lett.* **31**, L13101, doi:10.1029/2004GL020041.

Lupton, J. E. and Graham, D. (1991) Comment on "A ten-year decrease in the atmospheric helium isotope ratio possibly caused by human activity", by Y. Sano *et al. Geophys. Res. Lett.* **18**, 482–485.

Mamyrin, B. A., Anufriev, G. S., Kamensky, I. L. and Tolstikhin, I. N. (1970) Determination of the isotopic composition of atmospheric helium. *Geochem. Int.* **7**, 498–505.

Matsuda, J., Maruoka, T., Pinti. D. L. and Koeberl, C. (1996) Noble gas study of a philippinite with an unusually large bubble. *Meteorit. Planet. Sci.* **31**, 273–277.

Matsuda, J., Matsumoto, T., Sumino, H., Nagao, K., Yamamoto, J., Miura, U., Kaneoka, I., Takahata, N. and Sano, Y. (2002) The $^3He/^4He$ ratio of the new internal He Standard of Japan (HESJ). *Geochem. J.* **36**, 191–195.

Matsumoto, T., Chen, Y. and Matsuda, J. (2001) Concomitant occurrence of primordial and recycled noble gases in the Earth's mantle. *Earth Planet. Sci. Lett.* **185**, 35–47.

Oliver, B. M., Bradley, J. G. and Farrar, H., IV (1984) Helium concentration in the Earth's lower atmosphere. *Geochim. Cosmochim. Acta* **48**, 1759–1767.

Pierson-Wickmann, A.-C., Marty, B. and Ploquin, A. (2001) Helium trapped in historical slags: a search fro temporal variation of the He isotopic composition of air. *Earth Planet. Sci. Lett.* **194**, 165–175.

Sano, Y. (1998) Time rate of atmospheric $^3He/^4He$ change: Constraint from South Pacific deep seawater. *J. Sci. Hiroshima Univ. Ser. C* **11**, 113–118.

Sano, Y., Wakita, H., Makide, Y. and Tominaga, T. (1989) A ten-year decrease in the atmospheric helium isotope ratio possibly caused by human activity. *Geophys. Res. Lett.* **16**, 1371–1374.

Sano, Y., Wakita, H., Makide, Y. and Tominaga, T. (1991) Reply to Lupton and Graham. *Geophys. Res. Lett.* **18**, 486–488.