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Anne S. Palmer

Tas D. van Ommen

Mark A. J. Curran

Vin Morgan

Joe M. Souney

*See next page for additional authors*

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**Authors**

Anne S. Palmer, Tas D. van Ommen, Mark A. J. Curran, Vin Morgan, Joe M. Souney, and Paul Andrew Mayewski

# High-precision dating of volcanic events (A.D. 1301-1995) using ice cores from Law Dome, Antarctica

Anne S. Palmer,<sup>1</sup> Tas D. van Ommen,<sup>2</sup> Mark A. J. Curran,<sup>2</sup> Vin Morgan,<sup>2</sup>  
Joe M. Souney,<sup>3</sup> and Paul A. Mayewski<sup>3,4</sup>

**Abstract.** A record of volcanic activity over the period A.D. 1301-1995 has been extracted from three Law Dome ice cores (East Antarctica). The record dating is unambiguous at the annual level from A.D. 1807 to 1995 and has an uncertainty of  $\pm 1$  year at A.D. 1301. Signals from 20 eruptions are preserved in the record, including those of two unknown eruptions with acid deposition beginning in A.D. 1810.8 and A.D. 1685.8. The beginning of the ice core signal from the A.D. 1815 Tambora eruption is observed in the austral summer of A.D. 1816/1817. The mean observed stratospheric transport and deposition time to Law Dome from the eruption site is 1.5 years ( $\sigma = 0.6$  years) from 11 well-dated eruptions. The largest eruption observed in the Law Dome record has its maximum in A.D. 1460 with volcanic sulfate deposition beginning in the austral winter of A.D. 1459. This event is also observed in other ice core records and is attributed to the volcano Kuwae, with an eruption date in the range A.D. 1455.9-1459.9 if all sources of error are considered. This is at least three years later than the date previously ascribed by dendrochronological and historical studies.

## 1. Introduction

Cataclysmic volcanic eruptions inject large quantities of ash and gases into the upper troposphere and stratosphere. Sulfur dioxide ( $\text{SO}_2$ ), the main component of volcanic gases, is oxidized in the atmosphere to sulfate ( $\text{SO}_4^{2-}$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) via reactions with the hydroxyl radical and other oxidants [Cadle, 1980; Hamill and Kiang, 1977]. These stratospheric aerosol particles are then rapidly advected around the globe, several examples showing that volcanic clouds circle the Earth longitudinally in  $\sim 2$ -3 weeks. The transport time for volcanic aerosols to reach the polar regions is about 1-2 years and depends heavily upon the particular dispersion by winds at the time

of the eruption [Robock, 2000, and references therein]. The atmospheric residence lifetime of these aerosols is several years during which they can significantly alter the radiative balance and albedo of the Earth's atmospheric system. The recent explosive eruption of Mount Pinatubo in June 1991 ejected into the atmosphere an estimated  $18 \pm 2 \times 10^9$  kg of  $\text{SO}_2$  [Krueger *et al.*, 1995], which was rapidly converted to  $\text{H}_2\text{SO}_4$  aerosol particles [Bekki *et al.*, 1993]. The volcanic aerosol mass extended around the entire Earth by mid-1992 [Hitchman *et al.*, 1994], and global tropospheric and surface temperatures decreased by  $0.2^\circ$ - $0.7^\circ\text{C}$  [McCormick *et al.*, 1995; Jones and Kelly, 1996]. The volcanic fallout from explosive eruptions like Pinatubo is preserved in the polar ice sheets of Antarctica and Greenland, as first detected by Hammer [1977], and is used to mark reference horizons in the dating of low accumulation ice cores, including those from Vostok, Dome C, and South Pole.

The effect of explosive eruptions is also seen in historical and dendrochronological studies, for example, the Tambora eruption in A.D. 1815 is observed in some tree ring studies as a significantly narrowed ring in A.D. 1816, although other studies see no effects of this eruption [Sadler and Grattan, 1999, and references therein]. Historically, the year following the Tambora eruption has been referred to as the "year without a summer" with evidence from North and South America, Europe, Asia, and Australasia [Harrington, 1992].

The ice cores used in this study were drilled on Law Dome, a small ice cap with independent ice flow located

<sup>1</sup>Institute for Antarctic and Southern Ocean Studies, University of Tasmania, Hobart, Tasmania, Australia.

<sup>2</sup>Antarctic CRC and Australian Antarctic Division, Hobart, Tasmania, Australia.

<sup>3</sup>Climate Change Research Center, Institute for the Study of Earth, Oceans, and Space and Department of Earth Sciences, University of New Hampshire, Durham, New Hampshire, USA.

<sup>4</sup>Now at Climate Studies Center, Institute for Quaternary Studies, University of Maine, Orono, Maine, USA.

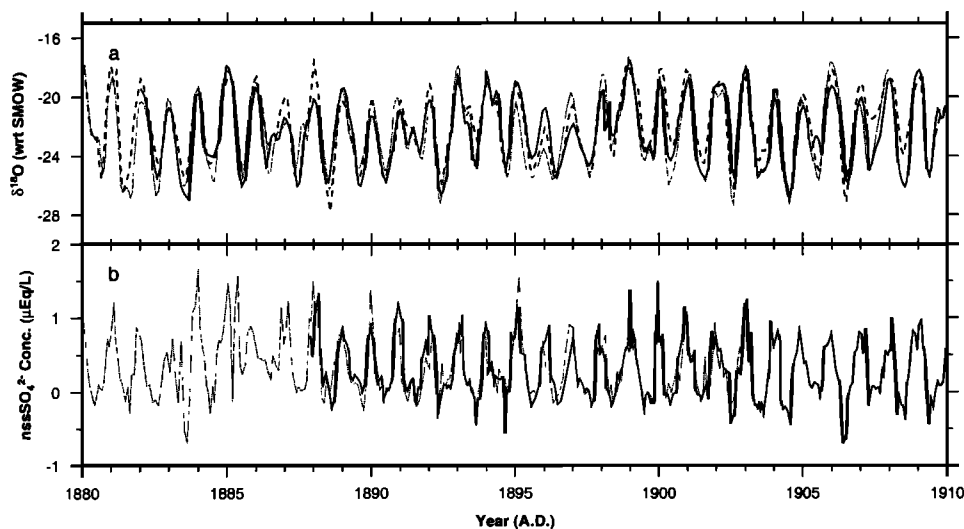
on the edge of the main East Antarctic ice sheet. The characteristics of the main drilling site on Law Dome, namely, Dome Summit South (DSS), include a high annual accumulation rate (0.7 m/yr ice equivalent), relatively low mean surface temperatures ( $-21.8^{\circ}\text{C}$ ), and low wind speeds (8.3 m/s) [Morgan *et al.*, 1997]. These site characteristics lead to highly resolved records with clear annual cycles in most measured parameters, giving very robust chronological control. In this study we have used the high precision to date the onset and explore the duration of volcanic deposition events over the period A.D. 1301-1995.

## 2. Methods

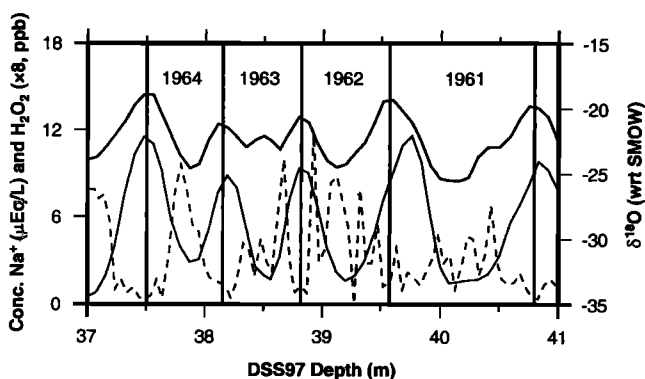
The volcanic record presented here is compiled from three ice cores: DSS97 (1.6 km southeast of DSS [Palmer *et al.*, 2001]), DSS99 (recovered in February 2000 from a site ( $66^{\circ}46'S$ ,  $112^{\circ}48'E$ ), 100 m south of DSS), and DSS [Morgan *et al.*, 1997]. These cores were sampled to span the periods A.D. 1888-1995, 1841-1888, and 1301-1841, respectively. Clear annual layers are observed for all three cores, and the records are dated using layer counting of oxygen isotope ratios ( $\delta^{18}\text{O}$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and major ions [e.g., van Ommen and Morgan, 1996, 1997; Curran *et al.*, 1998]. The  $\text{SO}_4^{2-}$  and sodium ( $\text{Na}^+$ ) traces show consistent mean and standard deviations near the core junctions and in the overlap section between DSS97 and DSS99. Figure 1a shows the  $\delta^{18}\text{O}$  records DSS97, DSS99, and DSS in this overlap section. The non-sea-salt sulfate ( $\text{nssSO}_4^{2-}$ , computed as discussed below) record for DSS97 and DSS99 in the same section is shown in Figure 1b. The agreement between these records has permitted unambiguous registration of the dating across the core boundaries. As well as reproducing measured concentrations of species

and subseasonal features, the separate records have a completely unambiguous match in depth, by virtue of the annual fluctuations in layer thickness. Any offset from the correct alignment in the overlap region results in a rapid loss of coherence between records after only a few cycles.

Long-term dating accuracy in records from this site is limited by the ability to discriminate seasonal cycles. Figure 2 shows a typical example with  $\text{Na}^+$  (dashed) reaching a maximum in the winter months, in contrast with the other species:  $\text{H}_2\text{O}_2$  (solid),  $\delta^{18}\text{O}$  (bold), and  $\text{nssSO}_4^{2-}$  (not shown) which peak in summer. Over the period A.D. 1807-1995 we have been able to unambiguously date the record on the basis of observed seasonal cycles, with corroborating data from another deep Law Dome ice core (DE08 [Morgan *et al.*, 1991]) and several shallower cores near the summit. The dating is occasionally complicated by autumn through spring precipitation events in which low-latitude air masses are rapidly advected over Law Dome, leaving a signal that mimics summer conditions in one or more parameters, most commonly  $\delta^{18}\text{O}$ . For example, in Figure 2 the isotope curve shows a "warm" hump in mid-1963. In this instance the possibility of a summer can be discounted on the basis of the absence of  $\text{H}_2\text{O}_2$ , the presence of elevated  $\text{Na}^+$ , and the improbably narrow annual layers that this would require. However, not all ambiguities can be resolved with complete certainty, and where this occurs, there is a tendency to count additional years. In the entire  $\sim 700$  year record we encounter just two ambiguities that may degrade dating. The first such occurrence in this record is the winter of A.D. 1806 which shows a trace chemistry signal indicative of a summer/winter cycle which is not counted because of a lack of other summer markers. This gives a possible age error of +1 year prior to A.D. 1807 (i.e., ages may



**Figure 1.** Overlap section of the DSS97 (solid curve) and DSS99 (thin) records for the species (a)  $\delta^{18}\text{O}$  and (b)  $\text{nssSO}_4^{2-}$ . The continuous  $\delta^{18}\text{O}$  DSS record (dashed) has also been included for comparative purposes.



**Figure 2.** Section of the DSS97 ice core record dated using annual layer counting. The  $\text{Na}^+$  record (dashed) reaches a maximum in the winter months, with  $\text{H}_2\text{O}_2$  (solid, scaled down by a factor of 8 for clarity), and  $\delta^{18}\text{O}$  (bold) peaking in the summer months. The year intervals have been labeled using a shaded line.

be 1 year older at most). There is one other ambiguous peak in the data at A.D. 1775. This is counted in the dating, leading to an uncertainty prior to A.D. 1776 of  $\pm 1$  year.

The DSS97 and DSS99 ice cores were sampled under clean conditions at 5 cm intervals, and a suite of ions measured using suppressed ion chromatography at the Antarctic CRC [Curran and Palmer, 2001]. The DSS core was sampled with a resolution varying from 5 to 10 cm, and trace ion measurements were carried out at the University of New Hampshire using techniques modified from Buck *et al.* [1992]. This sampling provided around 20 samples per year at the top of the DSS97 core compared with about 10–12 samples per year throughout the DSS core. Since the sampling density varies with depth, the data presented here have been smoothed and interpolated on to a uniformly spaced grid with 12 samples per year. The annual isotopic maximum has been used to define the “start” of each year. On average, this has the effect of placing the dating “year” about 10 days behind the calendar year [van Ommen and Morgan, 1996].

The  $\text{nss SO}_4^{2-}$  concentration has been calculated from total  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  concentrations using the sea-salt ratio:

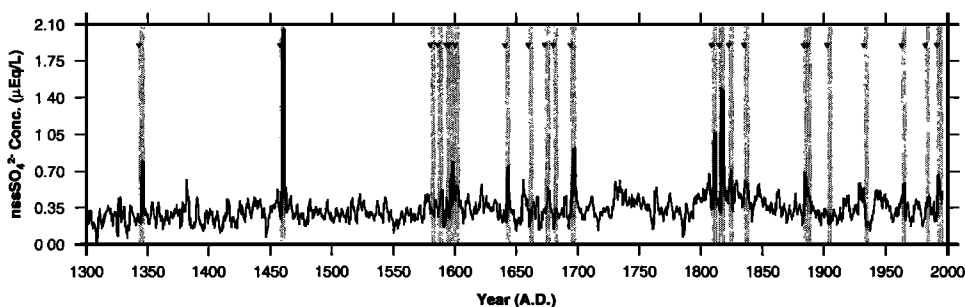
$$\text{nss SO}_4^{2-} = [\text{SO}_4^{2-}] - r[\text{Na}^+],$$

where  $r=0.1201$  is the sea-salt ratio of  $\text{Na}^+$  to  $\text{SO}_4^{2-}$  in seawater. Small negative values of  $\text{nss SO}_4^{2-}$  are calculated during the winter months due to sea-salt fractionation as reported at other coastal sites [e.g., Mulvaney *et al.*, 1993; Wagenbach *et al.*, 1998].

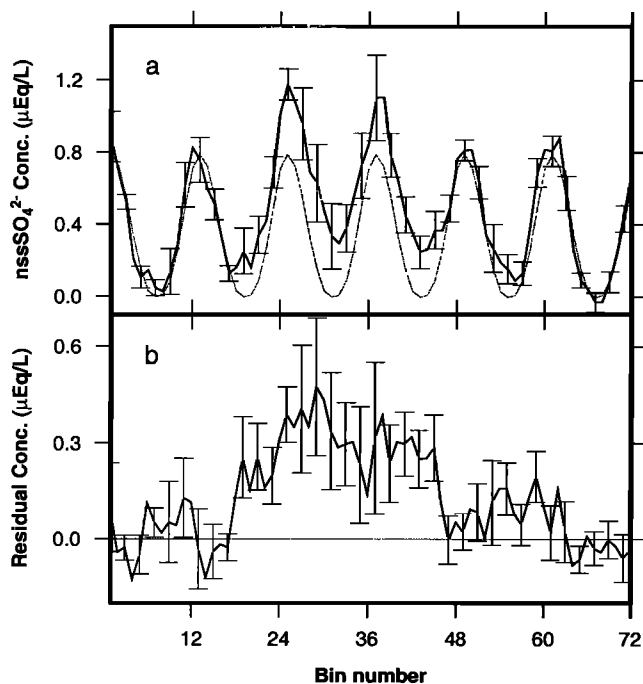
### 3. Results and Discussion

Figure 3 shows the  $\text{nss SO}_4^{2-}$  record for the period A.D. 1301–1995, smoothed with a 2 year moving average for illustrative purposes. The unsmoothed record is dominated by a strong seasonal cycle, which may be seen in Figure 4a. The summer maximum is primarily due to biogenic activity in the Southern Ocean. Other minor sources of  $\text{nss SO}_4^{2-}$  include volcanic eruptions, continental sources, and anthropogenic emissions.

The averaged  $\text{nss SO}_4^{2-}$  record in Figure 3 has a mean concentration of  $0.345 \mu\text{Eq/L}$  and shows several high concentration events due to volcanic fallout, with peak 2 year average values sometimes exceeding the mean summer maximum of  $0.788 \mu\text{Eq/L}$ . A total of 24 eruptions were examined in this study (Table 1). For nine of these the precise eruption date is not known, although the year is known for seven of them. Visual study of the  $\text{nss SO}_4^{2-}$  record leads to the identification of 20 volcanic signatures. Four eruptions, Cerro Azul, Santa Maria, TongKoko, and Long Island were not observed, the last of these due to a sampling gap where complete core sections were not available for trace ion analysis (dating continuity is not affected because we have  $\delta^{18}\text{O}$  and other data through this section). The other three eruptions are rarely observed in other Antarctic ice core records [e.g., Cole-Dai *et al.*, 1997; Delmas *et al.*, 1992], so it is not surprising that these eruptions are not evident in the Law Dome record. Two of the 20 volcanic signatures identified are from unknown volcanoes. The first began in A.D. 1810.8 and is well documented [e.g., Dai *et al.*, 1991], and the second, in A.D.



**Figure 3.** Two year smoothed  $\text{nss SO}_4^{2-}$  record (A.D. 1301–1995) and volcanic events. Small markers denote epochs of events from Table 1, and shaded bars indicate the 4 year interval after the eruption date.



**Figure 4.** (a) Mean annual cycles in  $\text{nssSO}_4^{2-}$ . Solid curve is the ensemble average for 6 years following the 10 well-dated volcanic eruptions noted in the text. To preserve coherence of the dominant seasonal cycle, all averages begin at month 1 in the year of the eruption. The thin curve is the mean for the entire A.D. 1301-1995 time period (excluding all 20 identified volcanic events). Alternate error bars are  $\pm 1\sigma$  standard errors in the mean over the 10 events, at each lag up to 6 years. (b) Mean residual  $\text{nssSO}_4^{2-}$  cycle computed as the difference between the curves in top panel.

1695.8, may be the same volcanic signature as seen in the Dyer Plateau (A.D. 1696-1697), Siple Station (A.D. 1695-1696), and GISP2 (A.D. 1694 and 1696) ice core records [Cole-Dai et al., 1997; Zielinski, 1995]. The GISP2 signals were attributed to eruptions in Iceland (A.D. 1693) and Japan (A.D. 1694) [Zielinski, 1995]; however, it is more likely that one of these events was a large eruption of global significance, although no such eruptions are noted in historical records [Simkin and Siebert, 1994]. The signal duration from the Huaynaputina eruption cannot be determined here due to unavailable trace ion data at A.D. 1603.5, although the start of the volcanic signature is observed. The Pinatubo and Cerro Hudson eruptions are not examined because their volcanic signatures in the Law Dome core overlap making any statistical interpretation difficult. For transport delay calculations, this leaves a suite of 10 well-dated eruptions with observed fallout: El Chichón, Agung, Tarawera, Krakatau, Cosiguina, Galunggung, Tambora, Gamkonora, Parker, and Ruiz.

We examined the significance of total  $\text{nssSO}_4^{2-}$  levels for nine of the 10 well-dated eruptions (Tambora was excluded from this significance test because its large mag-

nitude dominated the results). We employed a bootstrapping technique [von Storch and Zwiers, 1999] in which the  $\text{nssSO}_4^{2-}$  levels from the nine known eruptions were compared to 10,000 sets of nine randomly generated years from the record. We found that the nine eruptions show highly significant elevations in  $\text{nssSO}_4^{2-}$  when averaged over the 5 year period following the eruption year ( $0.465 \mu\text{Eq/L}$ ,  $p < 0.008$ ).

Generally, the volcanic signature is most evident in elevated winter levels following the eruption date. The winter envelope (defined as bins 6-8 where there are 12 bins per year) of the  $\text{nssSO}_4^{2-}$  signal is generally close to zero (mean concentration  $0.013 \mu\text{Eq/L}$ , Figure 4a), with some negative concentrations due to sea-salt fractionation. The ensemble average of posteruption periods for the 10 well-dated events is shown as the solid curve in Figure 4a. The  $\text{nssSO}_4^{2-}$  level in the winter of the eruption year was not significantly elevated ( $0.078 \mu\text{Eq/L}$ ,  $p > 0.1$ ). The winter concentrations for the second, third, and fourth years, following the eruption year, were significantly elevated for the 10 eruptions when compared to normal winter levels. The second winter had an average concentration of  $0.212 \mu\text{Eq/L}$  ( $p < 0.022$ ), the third winter  $0.204 \mu\text{Eq/L}$  ( $p < 0.023$ ), and the fourth winter  $0.243 \mu\text{Eq/L}$  ( $p < 0.017$ ), while the fifth winter was statistically indistinguishable from "normal" winters ( $0.065 \mu\text{Eq/L}$ ,  $p > 0.1$ ). Thus the majority of the volcanic  $\text{SO}_4^{2-}$  is deposited in the first four years following the eruption, where this spread reflects the rate of atmospheric removal, primarily by precipitation, and the timing of transport processes.

The average lag time between the eruption date and the elevation of volcanic  $\text{SO}_4^{2-}$  above mean levels in the ice was further examined in the  $\text{nssSO}_4^{2-}$  record using the ensemble of 10 eruptions (including Tambora). By examining the 1 year average  $\text{nssSO}_4^{2-}$  at varying lags following the eruption dates, we find significant elevations ( $p < 0.05$ ) for lag windows centered between 1.0 and 3.8 years inclusive. Hence the volcanic  $\text{SO}_4^{2-}$  is still present in the  $\text{nssSO}_4^{2-}$  record for 3 to 4 years after the eruption.

An estimate of the individual lags (as opposed to the mean ensemble lag) between the eruption dates and the onset of fallout was calculated using the residual  $\text{nssSO}_4^{2-}$  record, which emphasizes the volcanic signals. The mean seasonal cycle was calculated by removing all 20 known eruptions and then stacking the remaining record using 12 bins per year and calculating the average for each bin. This annual cycle was then subtracted from the  $\text{nssSO}_4^{2-}$  record to give the residual  $\text{nssSO}_4^{2-}$  trace. The start of the volcanic signal in this residual record was identified by a departure of the residual trace from the background noise level. These onset dates have been compared to eruption dates for the same set of ten well-dated eruptions listed above, plus Huaynaputina (for which onset was observed despite the data gap discussed earlier). This comparison gave a mean lag of 1.5 years ( $\sigma = 0.6$  years,  $N = 11$ ), with a range of 0.6 to 2.6

**Table 1.** The 24 Volcanic Eruptions Examined in the Law Dome Ice Core Record, A.D. 1301-1995

Volcano	Eruption Date <sup>a</sup>	Lat <sup>b</sup>	VEI <sup>c</sup>	Ice Date (year) <sup>d</sup>	Lag (year)	Signal Duration (year)
Pinatubo	14/6/1991	15	6	confused signal		
Cerro Hudson	12/8/1991	-46	5	confused signal		
El Chichón	3/4/1982	17	5	1984.8	2.6	1.5
Agung	17/3/1963	-8	4	1964.1	0.9	1.5
Cerro Azul	10/4/1932	-36	5	no signal		
Santa Maria	24/10/1902	15	6	no signal		
Tarawera	10/6/1886	-38	5	1887.8, noisy	1.3	1?
Krakatau	27/8/1883	-6	6	1884.7	1.0	2.5-3
Cosiguina	20/1/1835	13	5	1836.3	1.2	1.5-2
Galunggung	8/10/1822	-7	5	1823.3	0.6	2
Tambora	10/4/1815	-8	7	1816.8	1.6	2.5-3
Unknown				1810.8		2
Unknown				1695.8		2-3
TongKoko	1680	2	5	no signal		
Gamkonora	20/5/1673	1	5	1675.3	1.9	2.5
Long Island	1661	-5	6	ntid <sup>e</sup>		
Parker <sup>f</sup>	4/1/1641	6	6?	1642.5	1.5	2-2.5
Huaynaputina	19/2/1600	-17	6	1601.7	1.5	ntid
Ruiz	12/3/1595	5	4	1597.6	2.5	2
Raung	1593	-8	5	1596.1		1
Kelut	1586	-8	5	1588.3		1.5
Billy Mitchell	1580	-6	6	1584.4		1
Kuwae	1453	-6	6?	1459.5		3
Rangitoto	1350?	-37	?	1345.1?		2

Name of volcano, eruption date, latitude of volcano, and VEI information have been taken from *Simkin and Siebert* [1994] with the exception of the Parker eruption in 1641. Ice date, lag, and signal duration were calculated from the Law Dome ice core record.

<sup>a</sup>Eruption date is in the form day/month/year.

<sup>b</sup>Lat denotes the latitude of the volcano (in degrees) where southern latitudes are denoted as negative numbers.

<sup>c</sup>VEI denotes the volcanic explosivity index. Volcanoes are rated 0-8 in order of increasing explosivity.

<sup>d</sup>Start of the volcanic SO<sub>4</sub><sup>2-</sup> signal in the ice.

<sup>e</sup>ntid denotes "no trace ion data."

<sup>f</sup>Parker eruption in 1641 was previously attributed to the volcano Awu (C. Newhall, personal communication, 2001, and *Delfin et al.* [1997]).

years (see Table 1). The residual nssSO<sub>4</sub><sup>2-</sup> trace also shows the volcanic SO<sub>4</sub><sup>2-</sup> signature deposited in the ice (Figure 4b) with significant elevations above zero between bins 18 and 46, where there are 12 bins per year.

The lag between eruption and maximum in-ice concentration ranges from 1.0 to 3.8 years for the 10 well-dated events, and identification of this value is relatively insensitive to noise in the record. In contrast, the determination of the individual lags between eruption and onset of volcanic SO<sub>4</sub><sup>2-</sup> is sensitive to noise and hence so is the average of 1.5 years. Detection of the onset, i.e., the point at which the volcanic signal can be distinguished from background, depends on the time required for the volcanic signal to increase above the noise and on the nature of the background signal itself. The volcanic signals observed here display a rapid increase in nssSO<sub>4</sub><sup>2-</sup> values, suggesting that the lag introduced before identifying onset is unlikely to be more than a month or two (note also that precipitation events occur with sufficient regularity at this site to preserve signals with a monthly resolution, on average [e.g., *van Ommen and Morgan*, 1997; *McMorrow et al.*, 2001]). Systematic influences on the background signal from fraction-

ation effects could also potentially delay detection of volcanic sulfate, and to check this, we have conducted tests using fractionation models being developed as part of a separate study. These tests also showed that fractionation did not lead to appreciable change in the lags quoted here, probably again due to the rapid nature of increases once deposition begins.

The large range of individual transport lags calculated illustrates the dependence of this variable on the wind distribution patterns at the time of the eruption. Two examples of this are the El Chichón and Agung eruptions. The El Chichón (17°N) eruption in 1982 has a "long" lag time of 2.6 years. This was a sulfur-rich eruption which penetrated the stratosphere to 26 km and occurred when the quasi-biennial oscillation (QBO) went from easterly to westerly in the lower stratosphere which may be one factor explaining the confinement of the plume to mostly north of the equator [*Labitzke and McCormick*, 1992]. Thus the volcanic SO<sub>4</sub><sup>2-</sup> from this eruption would have taken longer to reach Antarctica and a weaker signal would be observed in the ice compared to Greenland ice cores. The second example, Agung, with a "short" lag time of 0.9 years, occurred at

the same phase in the QBO as El Chichón; however, this volcano is located at latitude 8°S and was unusual with most of the volcanic plume remaining south of the equator. This contributed to a shorter transport time and a stronger signal in Antarctic ice cores compared with Greenland ice cores [Legrand and Wagenbach, 1999, and references therein].

Preliminary dating of the DSS core had the fallout from the A.D. 1815 Tambora eruption at A.D. 1815/1816 [Morgan et al., 1997], in agreement with other ice core records [e.g., Delmas et al., 1992; Cole-Dai et al., 1997; Langway et al., 1995]. However, the revised multiparameter, multicore dating of the Law Dome record presented here places the beginning of the Tambora fallout in late winter A.D. 1816 with the volcanic SO<sub>4</sub><sup>2-</sup> dominating the seasonal cycle by the summer of A.D. 1816/1817. This is the first time the Tambora volcanic fallout has been accurately dated to A.D. 1816/1817 using ice core records (Thompson and Mosley-Thompson [1992] ascribed a date of A.D. 1817-1819 for the Tambora fallout from a Siple Station core, although this was revised to the 1815/1816 summer in subsequent papers [e.g., Cole-Dai et al., 1997]).

The eruption of Kuwae in the South Pacific was described by Monzier et al. [1994] as the most powerful event in the last 10,000 years. Monzier et al. [1994] quoted a date for the eruption of A.D. ~1425 based on radiocarbon and historical evidence. More precise dating using historical events by Pang [1993] gave a date of A.D. 1453, which is supported by dendrochronological studies [e.g., Briffa et al., 1998]. The largest volcanic signature of the Law Dome record begins a little later in A.D. 1459.5 and dominates the nss SO<sub>4</sub><sup>2-</sup> record for several years afterward. Considering the ±1 year dating error at A.D. 1459 and the range of individual transport lags (0.6-2.6 years), we calculate an eruption date for Kuwae ranging between A.D. 1455.9 and 1459.9, some three years after the historical and dendrochronologically ascribed date. Other polar ice cores show a volcanic signature between A.D. 1450 and A.D. 1464, with the range attributed to timescale errors, though the well-dated cores from Crete and GISP2, Greenland, show an eruption signature in A.D. 1459/1460 [Hammer, 1980; Zielinski, 1995] in agreement with the Law Dome chronology.

#### 4. Conclusion

The dating of paleorecords, and particularly ice cores, from low-accumulation sites relies considerably upon knowledge of dates and transport lags for identification of the volcanic eruption signal. This study provides new evidence, which reduces uncertainties in dating key volcanic events during the last 700 years. In particular, it is evident that the SO<sub>4</sub><sup>2-</sup> from some eruptions may take close to 2 years to appear (e.g., Tambora A.D. 1816/1817) and persist for several seasons. Twenty volcanic eruptions were identified in the seven

century Law Dome ice core record. The largest volcanic signature spans 3 years and starts in winter A.D. 1459 and is probably due to the explosive eruption of Kuwae, which had been dated using historical and tree ring records to A.D. 1453. Using the Law Dome record, we believe the Kuwae eruption occurred between A.D. 1455.9 and A.D. 1459.9.

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- M. A. J. Curran, and V. Morgan, and T. D. van Ommen, Antarctic CRC and Australian Antarctic Division, GPO Box 252-80, (mark.curran@utas.edu.au; vin.morgan@utas.edu.au; tas.van.ommen@utas.edu.au)
- P. A. Mayewski, Climate Studies Center, Institute for Quaternary Studies, Sawyer Environmental Research Laboratory, University of Maine, Orono, ME, 04469-5717, USA.
- A. S. Palmer, Institute for Antarctic and Southern Ocean Studies, University of Tasmania, GPO Box 252-77, Hobart, Tasmania, Australia. (anne.palmer@utas.edu.au)
- J. M. Souney, Climate Change Research Center, Institute for the Study of Earth, Oceans and Space and Department of Earth Sciences, University of New Hampshire, Durham, N.H., 03824, USA.

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