Reports

Historic Volcanism, European Dry Fogs, and Greenland Acid Precipitation, 1500 B.C. to A.D. 1500

Abstract. *Historic dry fogs in Europe, acid precipitation in Greenland, and major explosive volcanic eruptions correlate well with each other between 1500 B.C. and A.D. 1500. European (Mediterranean and Icelandic) volcanic eruptions appear to be the source of at least five of the nine largest acidity signals found in Greenland ice for this period. Between 152 B.C. and A.D. 43, eruptions of sulfur-rich Mount Etna probably supplied about 15 percent of the smaller acidity signals.*

A continuous record of past explosive volcanism in the world can be determined at a single site by two very different methods. One method is based on measuring acidity signals in annual layers of polar ice (*1*). Large peaks of acidity represent deposition of acid aerosols generated by explosive eruptions which, if distant, must have affected the global atmosphere but, if nearby, might have had only regional atmospheric impact. Tropospheric winds will usually carry the low-lying part of the volcanic cloud only a short distance before the particles fall out, but stratospheric winds will inevitably extend the upper part longitudinally around the globe and carry the whole mass poleward as it slowly settles out. Therefore, in order to use the ice-core acidity record as a quantitative measure of global volcanic aerosols, the location of the eruption source must be determined.

Modern eruptions that have generated enough aerosols to produce major acidity peaks in Greenland ice are also known to have produced other atmospheric effects, such as haze or dry fog, dimming of the sun, and peculiar optical phenomena, as well as possible climatic cooling (*2*). These effects have been reported in Europe after large local eruptions, such as that of Laki (Iceland) in 1783 (*3*). In addition, very large eruptions at distant localities, like the 1815 explosion of Tambora (Indonesia), can produce similar atmospheric anomalies as far away as Europe and eastern North America (*4*). Historical records, therefore, provide a second source of information about distant volcanism. For many modern eruptions (those since A.D. 1500), reports of atmospheric phenomena have been compiled and described (*2, 5*). For earlier eruptions, however, no such compilation is available. We searched the extant European (and some Near Eastern) literature of the period 1500 B.C. to A.D. 1500 for accounts of atmospheric aftereffects and local volcanic eruptions that might have caused these aftereffects.

We compared years of major eruptions derived from historical sources (*6*) with years of the largest acidity peaks (> 4 μeq of H^+ per kilogram of ice) in Greenland ice reported by Hammer *et al.* (*1*). Our search of the literature was comprehensive only for the period 735 B.C. to A.D. 630; for the earlier and later years discussed, we were guided by the work of Hammer *et al.* (*1*) as to which periods to examine in detail. (Relevant reports on events before ~ 735 B.C. may be mostly legendary in any case.) Most eruption years were determined through the reported atmospheric aftereffects of the eruptions; in about half the cases, however, a specific volcano was pinpointed as the likely source (Table 1). The table omits the period A.D. 44 to ~ 540, for which ice-core data are unavailable.

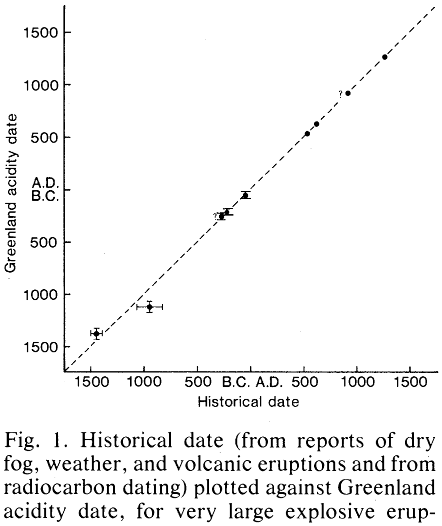

Fig. 1. Historical date (from reports of dry fog, weather, and volcanic eruptions and from radiocarbon dating) plotted against Greenland acidity date, for very large explosive eruptions, 1500 B.C. to A.D. 1500. Ice-core acidity information is not available for the period A.D. 44 to 540.

There is a strong correlation between the two sets of data on eruption years (Fig. 1). Since, however, our historical compilation can be considered a completely independent source only between 735 B.C. and A.D. 630, we have performed a significance test exclusively on this period, taking into account the known uncertainties in the ice-core dates that arise from the difficulty of counting the annual layers. We consider the probability P of obtaining s successes in r random, simultaneous selections from a list of n different years, of which m specified years are of interest

$$P = \binom{m}{s}\binom{n-m}{r-s}\Big/\binom{n}{r}$$

The years of interest here are those of high acidity, including all years lying within ±1 standard deviation of the most probable year for each acidity signal; these years total $m = 200$, with a gap (no ice-core data) between A.D. 44 and 540 omitted from the count and the years that overlap counted only once. Since we also have $n = 880$, $r = 5$, and $s = 4$ (where r and s refer to the historical eruption years and we have conservatively not regarded 270 B.C. as a "success"), we obtain $P = 0.010$. Thus the probability that the apparent correlation is accidental is negligible. We may conclude from this (i) that atmospheric aftereffects alone can be used to infer large volcanic eruptions, even in early historical times; (ii) that the largest acidity signals in old Greenland ice are due to these very same eruptions; and (iii) that early historical records can be used to date precisely the largest Greenland acidity signals and thereby help establish an accurate, premodern ice-core chronology. Our analysis strongly supports the conclusions of Lamb and Hammer (*2*) for the modern period and extends the time span of their analysis by many times.

According to the data in Table 1, European eruptions dominate the ice-core record. Even with the questionable 217 B.C. Vesuvius eruption not counted, five of the nine eruption years between 1500 B.C. and A.D. 1500 were times of great European eruptions: three in the Mediterranean area and two in Iceland. These results are partly understandable in view of Europe's (especially Iceland's) proximity to Greenland. Although the total of nine detected great eruptions does not represent the complete worldwide incidence of great eruptions during this period, it does reflect a

Table 1. Years of major volcanic eruptions determined by several different methods, from 1500 B.C. to A.D. 1500. There is a gap in the table (no ice-core data) between A.D. 44 and A.D. ~ 540. The survey of historical records is complete only between 735 B.C. and A.D. 630. Abbreviations: A, archeology and legend; D, dry fog; E, eruption column; F, distant ash fall; O, optical phenomena; R, radiocarbon; and W, weather.

Largest Greenland acidity peaks	Historical data		
Year*	Year	Volcano	Method
1390 ± 50 B.C.	1500–1400 B.C.	Thera (Greece)	A, R*
1120 ± 50 B.C.	950 ± 130 B.C.	Hekla (Iceland)	R*
260 ± 30 B.C.	270? B.C.	?	W?
210 ± 30 B.C.	217–216 B.C.	Vesuvius (Italy)?	D, E?, O?, F?
50 ± 30 B.C.	44 B.C.	Etna (Italy)	D, W, E, O, F
A.D. 540 ± 10	A.D. 536	Rabaul (New Britain)?	D, W, R?
A.D. 623 ± 3	A.D. 626	(Mediterranean)	D, W, F
A.D. 934 ± 2	A.D. 934?	Eldgjá (Iceland)	A,* W?
A.D. 1258 ± 1	A.D. 1258	?	D, W

*Hammer *et al.* (*1*).

continual and uniform sampling at one site, confirming that long-term time studies of historic explosive volcanism can be made.

Smaller European eruptions also seem to have left detectable signs in Greenland ice. Hammer *et al.* (*1*) published a complete record of "unambiguous" (> 1.5 μeq of H^+ per kilogram) acidity signals for the limited period 152 B.C. to A.D. 43. Our record of historical Mediterranean eruptions of moderate to large size (*6*) indicates that dates of known eruptions (which are all due to Mount Etna) are 141, 135, 126, 122–121, 50–49, 44, 36, and 32 B.C. and A.D. 38–40. To compare these dates with those of the acidities, it is necessary to adjust the zero-point of the ice-core dates (following our preceding analysis) so that the large acidity peak at 50 B.C. (±30 years) corresponds to the historical eruption year 44 B.C. when the great dry fog appeared in Europe (*7*). Allowing for a time lag of up to 1 year for the transport of acid aerosols from the Mediterranean to Greenland (*1*), we find that seven of the nine eruptions of Etna between 152 B.C. and A.D 43 appear to correlate exactly with Greenland acidity peaks. If we assume there are no errors in the ice-core dates other than the zero-point error (*8*), then by setting $m = 55$, $n = 195$, $r = 9$, and $s = 7$, we obtain $P = 0.002$ as the (very small) probability that so many coincidences could happen by chance. Hence a single volcano, Mount Etna, probably produced about 15 percent of the unambiguous acidity peaks between 152 B.C. and A.D. 43. Field studies, including approximate radiocarbon dating, confirm the volcano's greater explosivity during classical antiquity as compared with recent centuries (*9*). Mount Etna, moreover, releases an exceptionally large proportion of sulfur among its discharged gases (*10*), so that an Etnan eruption that is only moderately explosive by global standards could produce a quite noticeable sulfuric acid signal in Greenland ice. Tropospheric and stratospheric winds need not (though they possibly may) follow a favored route between the Mediterranean and Greenland, but little is known about this question (*11*).

The relative dominance of European eruptions in the ancient ice-core record contrasts with the relative unimportance of European eruptions in modern times (Fig. 2). We are able to suggest two reasons for this difference. First, Northern Hemisphere explosive volcanism outside Europe seems to have been significantly less vigorous during antiquity than in recent centuries, as Fig. 2 indicates; smaller eruptions appear to have followed the same trend, as indicated by the fact that, during the period 152 B.C. to A.D. 43, only 55 acidity peaks in Greenland ice exceed 1.5 μeq of H^+ per kilogram, whereas 82 acidity peaks do so from A.D. 1778 to 1972 (*1*). This trend does not seem to reflect greater difficulty in identifying and measuring the older ice layers and their acidities—problems which have reportedly been overcome (*1, 12*) (for example, seven acidity peaks > 4 μeq of H^+ per kilogram were detected for the eighth millenium B.C.). The statistics on known volcanic eruptions support the suggestion that large areas of the world can experience centuries-long periods of relative volcanic inactivity, only to return to a state of greater activity later (*13*). Second, it is possible that most of the largest explosive Northern Hemisphere eruptions outside Europe during antiquity were relatively poor in sulfur content, and hence are underrepresented in Greenland ice. In support of this idea, we note that, although the silica content of magma is easily measured and sulfur is not, the relative abundances of these two elements tend to be inversely correlated in known cases (*14*). Therefore, it is significant that the European volcanoes Etna, Laki, and Lanzarote (Canary Islands) have produced in modern times large lava-flow eruptions of low silica content, followed by strong acidity peaks in Greenland ice and dry fogs in Europe (*1, 2*), whereas the more explosive, high-silica eruptions of Bezymianny (Kamchatka) and Santa Maria (Guatemala) failed to produce large acidity peaks in Greenland ice (*1, 15*).

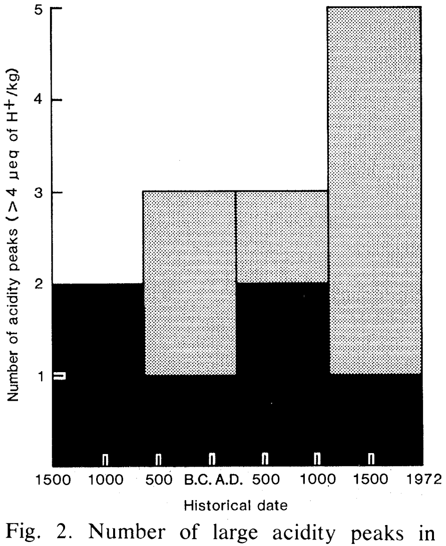

Fig. 2. Number of large acidity peaks in Greenland ice for four equal subdivisions (868 years each) of the historical period 1500 B.C. to A.D. 1972. Black area represents the acidity peaks attributed with some certainty to European volcanic eruptions. (Ice-core acidity information is not available for A.D. 44 to 540.)

Our results could be even more striking if a detailed ice core were available for the missing period A.D. 44 to 540. Vesuvius is known to have experienced cataclysmic eruptions in A.D. 79 and 469 to 474 (*6*). Unless these eruptions were sulfur-poor, they should be easily detected as large acidity spikes in Greenland ice. The eruption of A.D. 469 to 474 also appears to have generated an extensive dry fog in Europe (*6*).

So far, our findings, in conjunction with those of Hammer *et al.* (*1*), indicate that European volcanic eruptions produced at least six of the 13 largest acidity peaks recognized in Greenland ice during the past 3500 years. The record of European dry fogs and Greenland ice acidities will be useful in computing global atmospheric aerosol loading in studies of volcanic effects on climate.

RICHARD B. STOTHERS
MICHAEL R. RAMPINO
NASA/Goddard Institute for Space Studies, 2880 Broadway, New York 10025

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7. The effects of the eruption lasted 3 years and were observed also in China; the *Han shu* records (for May to June 43 B.C.): "The sun's color was pale blue and there were no shadows (on the ground). At noon exactly there were shadows but no brightness." The translation is taken from D. H. Clark and F. R. Stephenson, *Q.J.R. Astron. Soc.* **19**, 387 (1978).
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16. We thank the two referees for their helpful comments on the manuscript and C. U. Hammer for supplying detailed copies of his acidity records and for a valuable discussion. Supported in part by a NASA grant to Columbia University.

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Rates of Hydrothermal Reactions

Abstract. *The rates of reactions of silicates and aqueous fluids follow zero-order kinetics controlled by the reacting surface area with the rate constant given by the equation:* $\log k \simeq -2900/T - 6.85$, *where* T *is temperature and where* k *has the unit's gram-atoms of oxygen per square centimeter per second. This expression appears to hold for all silicates and for reactions involving dissolution, fluid production, or solid-solid transformations in the presence of a fluid of moderate to high* pH.

The rate relations of hydrothermal reactions are of considerable interest in geologic and materials sciences. A full understanding of these processes would enable us to predict weathering phenomena, reactions in geothermal and metamorphic systems, and the aqueous dissolution behavior of, for example, nuclear waste–bearing ceramics. In the course of reviewing published data (*1–19*) on reaction rates, we have discovered a general Arrhenius relation between reaction rate and temperature that appears to hold over temperatures from 25° to 710°C. It also holds for a large number of different silicate and related mineral species.

In the most detailed studies of mineral reaction rates (*1–7*), investigators have examined low-temperature dissolution phenomena of the type associated with weathering at the earth's surface. Such reactions may be represented as follows:

$$\text{mineral} + H_2O \rightarrow \text{aqueous solution} + \text{secondary solids} \quad (1)$$

Although many experimenters have found complex dissolution behavior, it has recently been shown (*4, 20, 21*) that apparent nonlinear relations are artifacts of sample preparation. Once fine-grained material is removed, dissolution follows a zero-order rate relation (*3–7*) controlled by the reacting surface area:

$$\frac{dm}{dt} = k_{\text{dis}} \quad (2)$$

The rate of removal of mass from the dissolving mineral (dm/dt, in moles per square centimeter per second) is therefore a constant at fixed temperature, pressure, and activities of solution species. The rate constant, k_{dis}, is, however, a function of temperature (*1, 7, 21*) and is pH-dependent in acidic solutions. Dissolution rates increase with increasing temperature (*1*) and with decreasing pH. At moderate to high pH [> 5 for feldspar at 25°C (*4, 20*)], however, the dissolution rate becomes pH-independent. The reason for the change in behavior reflects the nature of the rate-determining step. At high activities of H_3O^+ the hydrolysis process involves H_3O^+ in the rate-determining step, whereas at very low activities of this species undissociated solvent (H_2O) is the agent of hydrolysis (*20*). The extent of the pH-dependent region varies from phase to phase (*4, 20, 21*), presumably because of different interfacial properties and extents of H_3O^+ adsorption.

Most dissolution experiments have been performed in the temperature range from 0° to 90°C, with a few studies (*1, 2, 7*) extending up to 300°C. The higher temperature experiments were predominantly directed toward establishing equilibrium rather than toward estimating kinetic properties of reactions. Many of these "equilibrium" studies may be used to estimate reaction rates, provided certain assumptions are made about the nature of the rate-controlling process.

Let us consider a generalized high-temperature reaction involving solid and fluid phases:

$$\text{phase A} + \text{phase B} = \text{phase C} + \text{phase D} \quad (3)$$

Such reactions are generally studied in order to establish the temperature and pressure conditions of equilibrium between phases A, B, C, and D, one of which is typically a fluid. One of the most precise and successful methods of determining equilibrium in such cases (*8–19, 22*) is to use a fine-grained matrix of all but one of the product and reactant solids and a single crystal of the remaining phase. The experimental method requires only a few percent of fluid so that the production of fluid species is minimized. One then determines the direction of reaction by weighing the single crystal before and after the experiment to determine whether it is in the stable or unstable assemblage (Fig. 1). This method yields equilibrium at the point of zero weight change and, near equilibrium, an approximately linear relation between weight change and temperature (Fig. 1) (*23*). Linear behavior close to equilibrium is predicted by transition state theory (*20, 23–25*) which, under these circumstances, yields an equation of the form

$$\frac{dm}{dt} = \frac{k_r\,[\Delta S_r(T - T_{\text{eq}})]}{RT_{\text{eq}}} \quad (4)$$

where k_r is the rate constant for the forward reaction at the equilibrium temperature T_{eq} (in kelvins), ΔS_r is the overall entropy change of the reaction, and R is the gas constant. Using Eq. 4, we have extracted k_r values for a large number of single-crystal studies (*8–19*) performed at temperatures from 300° to 710°C (Fig. 2). Values of ΔS_r were computed from data of Helgeson *et al.* (*26*). Values of ΔS_r for reactions in H_2O–CO_2 were corrected for nonideal fluid behavior. The linear approximation breaks down far from equilibrium because of the temperature dependence of k_r (*23*) (Fig. 1). Neverthe-