

likelihood per se, it nonetheless leads one to ask how these simple models perform in both simulations and with real data sets, when the assumptions may not be met. Specifying the details of a probability model (the maximum likelihood approach) does appear to be an advantage when the model is correct, as shown by the high performance of maximum likelihood in relevant simulation studies (7). However, the experimental data indicate that maximum likelihood can also perform more poorly than other methods when its assumptions are violated (as with the restriction-site data of our experimental viral lines) (1, 8). Presumably, Edwards' response would be that we need a better model of restriction-site change. Although we certainly encourage the development of better (more realistic) evolutionary models, maximum likelihood approaches are already computationally limiting, and no maximum likelihood models have been developed for many kinds of data. Given the limitations of our knowledge about how sequences and other characters evolve, and given the computational limitations of maximum likelihood, we see an obvious role for simulations and experimental studies to evaluate the performance of competing methods under a wide variety of conditions. In other words, we accept Edwards' criticism: We are interested in knowing which methods are likely to be correct under a wide variety of conditions and are not limited to asking which methods give credible answers if the specified model is true. Given that specified models are probably never correct in all their details, we see this as a necessary means of assessing the accuracy of phylogenetic methods as they are applied to real world problems.

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The GISP Ice Core Record of Volcanism Since 7000 B.C.

Zielinski *et al.* discuss the possibility that the volcanic eruptions they discern in the GISP2 ice core may be correlated with climatic effects and cultural responses in prehistory. Such correlation is impeded because Zielinski *et al.* do not correct ^{14}C dates for known eruptions to calendar years. This error invalidates their identification of ice core "events" with particular prehistoric eruptions. For example, Zielinski *et al.* link the event of 4803 B.C. to the eruption of Mount Mazama, Oregon, dated by ^{14}C to 4895 plus 50 B.C. However, in calendar years, the Mazama eruption dates to about 5700 B.C. (1). Therefore, the most likely indication of this eruption in the Greenland ice record may be the event of 5676 B.C., which produced a huge sulfate residual of 654 ppb.

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G. A. Zielinski *et al.* (1) present a detailed record of the volcanic contribution to sulfate concentrations in the GISP2 ice core. Table 1 of their report compares SO_4^{2-} peaks (dated by annual layer counting) with documented volcanic eruptions over the past 2000 years. They then attempt [table 2 in (1)] to link peaks in the earlier section of the record with radiocarbon-dated eruptions that were chosen from the compilation of Simkin *et al.* (2) on the basis of high Volcanic Explosivity Index (VEI).

Most of the eruption dates labeled as "B.C." in table 2 in (1) were calculated by subtracting 1950 years from radiocarbon ages, rather than by using standard radiocarbon calibration procedures (3). [Most of the radiocarbon dates in (2) are treated in the same manner.] Aside from possible counting errors, ice layer counting years are real (calendar) years, whereas radiocarbon years are artificial constructs. Radiocarbon dates must be calibrated to take into account both the use of a 5568-year half-life for ^{14}C (rather than the true value of 5730 years) and the effects of changing amounts of radiocarbon in the atmosphere (3), before comparisons can be made with ice core chronologies.

We have used a standard calibration pro-

gram (4) to generate calibrated dates from the radiocarbon data in table 2 of the report by Zielinski *et al.* (Table 1). Calendar dates are shifted by amounts ranging from a few years at 1 B.C. to around 800 years for the period before 3000 B.C., and most of the proposed linkages between specific volcanic eruptions and particular SO_4^{2-} peaks are invalidated. Although not shown, radiocarbon-dated eruptions in the 100 to 700 A.D. range in table 1 in (1) also require correction (by 100 to 150 years, to younger calendar ages).

The effects of calibration can be demonstrated with the use of two of the better-dated eruptions in the record: Aniakchak II and Mazama. The Aniakchak radiocarbon date (3430 ± 70 B.P.) yields two possible calendar year age ranges: 1872 to 1840 B.C. and 1780 to 1626 B.C. Sulfur emissions from Aniakchak are estimated (5) to have been the largest of a group of four eruptions (including Santorini) that are radiocarbon dated to around 3400 B.P. The new calendar dates for Aniakchak overlap with the 213-ppb SO_4^{2-} peak at 1695 B.C., the largest sulfate peak in almost four millennia. Similarly, calibration gives a calendar age range of 5713 to 5630 B.C. for Mazama; the eruption occurred more than 700 years before the date given in (1). This age range includes the 654-ppb SO_4^{2-} peak at 5676 B.C., one of the largest peaks in the record.

Thus, using calibrated ages, the prominent sulfate peaks at 1696 B.C. and 5676 B.C. can now be associated with known, large eruptions. Detailed examination of our Table 1 and other large peaks in the sulfate record (1) suggests that the use of these standard calibration procedures significantly improves the overall match.

Notwithstanding the above, we believe that associations between radiocarbon dated volcanic events and sulfate spikes, and their implications, should be addressed cautiously. Radiocarbon dating uncertainties and calibration curve plateaus can lead to large calendar age ranges. Given such uncertainties, almost any radiocarbon date ≤ 8000 B.P. can be associated with at least one (and often several) of the many SO_4^{2-} peaks. Restricting the comparisons to the largest VEI eruptions and SO_4^{2-} peaks provides a stronger constraint, but is still problematic, given the "hits" obtained with an uncalibrated chronology (1). Also, miscounting of ice layers, or radiocarbon dating problems (discussed in 5-7), may introduce systematic dating errors.

Furthermore, magma type (8) or aerosol

Table 1. Calibrated dates for eruptions in table 2 of Zielinski *et al.* (1).

Eruptive event and location	Year of event (B.C.) from Zielinski <i>et al.</i> (1)	¹⁴ C Date of event (¹⁴ C years B.P.)*	Calibrated age ranges† (years B.C. except where noted)
Sheveluch, Kamchatka, Russia	50 ± ?	2000 ± ?‡	116 B.C.–126 A.D.
Vulcano, Italy	183§	—	same
Okmok, Alaska, USA	450 ± 200	2400 ± 200	791–356 : 289–246
Krafla, Iceland	550 ± ?	2500 ± ?‡	783–513
Yantari, Alaska, USA	800 ± 500	2750 ± 500	1521–356
Bardarbunga (Veidivotn), Iceland	1150 ± 100	3100 ± 100	1455–1252 : 1245–1210
Aniakchak, Alaska, USA	1480 ± 10	3430 ± 70	1872–1840 : 1780–1626
Santorini (Minoan Eruption), Greece	1623–1627	3309 ± 17¶	1607–1558 : 1542–1526
Long Island, New Guinea	2040 ± 100	3990 ± 100	2619–2324
Hekla (H-4), Iceland	2310 ± 20#	—	same
Black Peak, Alaska, USA	2485 ± 300	4435 ± 300	3512–3396 : 3394–2858 : 2817–2687
Akutan, Alaska, USA	3250 ± 200	5200 ± 200	4232–3795
Towada, Japan	3450 ± 150	5400 ± 150	4358–4040
Kikai, Ryuku, Japan	4350 ± ?	6300 ± ?‡	5331–5198 : 5180–5134 : 5122–5078
Avachinsky, Kamchatka, Russia	4400 ± ?	6350 ± ?‡	5427–5397 : 5384–5219
Masaya, Nicaragua	4550 ± ?	6500 ± ?‡	5488–5316
Mazama, Oregon, USA	4895 ± 50	6845 ± 50	5713–5630
Hekla (H-5), Iceland	5050 ± ?**	6185 ± 100	5228–5031 : 5028–4996
Hangar, Kamchatka, Russia	5040 ± 75	6990 ± 75	5939–5912 : 5877–5744
Kizimin, Kamchatka, Russia	5300 ± 300	7250 ± 300	6373–5803
Tao-Rusyr, Kurile Islands	5550 ± ?	7500 ± ?‡	6407–6218
Karymsky, Kamchatka, Russia	5700 ± 50	7650 ± 50	6481–6408
Vesuvius, Italy	5960 ± 100	7910 ± 100	6997–6919 : 6898–6839 : 6786–6606
Pauzhetka, Kamchatka, Russia	6220 ± 150	8170 ± 150	7422–7002
Bardarbunga (Veidivotn), Iceland	6650 ± 50	8600 ± 50	7690–7667 : 7629–7535
Towada, Japan	6650 ± 300	8600 ± 300	7966–7309

*Except where noted, the ¹⁴C dates were obtained by adding 1950 to the eruption dates given in (1).
 †¹⁴C dates were calibrated with the use of method B in (4). The calibrated age ranges correspond to the radiocarbon dates and their 1σ uncertainties. In the few cases where multiple intercepts with the radiocarbon calibration curve occurred, we have excluded additional age ranges corresponding to less than 5% of the total 1σ probability.
 ‡In those cases in which a ¹⁴C date uncertainty range was not given in (1), an uncertainty of ±100 years was assigned.
 §Eruption is dated historically (10).
 ||Original radiocarbon dates (11) indicate a ±70 year uncertainty range, not the 10-year range quoted in (1, 2, and 11).
 ¶The radiocarbon date used for the Santorini eruption was obtained by Hammer *et al.* (12) [see also reference 32 in (1)]. The date has been recalibrated with the use of the most recent calibration data sets (3).
 #Calibrated age (J. Pilcher, V. A. Hall, F. G. McCormac, paper presented at the 15th International Radiocarbon Conference, 15 to 19 August 1994, Glasgow, Scotland).
 **Calibrated age. We have recalibrated the original 6185 ± 100 B.P. radiocarbon date (13) with the use of the most recent calibration data sets (3).

transport efficiency may be more important than VEI in determining atmospheric loading and deposition of sulfate. For example, none of the five VEI ≥ 5 events in Kamchatka during the past 2000 years [table 1 in (1)] can be associated with SO₄²⁻ peaks greater than 150 ppb. The early Holocene Kamchatkan eruptions of Kizimin and Karymsky involved dacitic magmas (6) and may have been relatively poor sulfur emitters. Hence, if these latter eruptions were truly the sources for some of the large SO₄²⁻ peaks from the early Holocene, increased transport efficiency to the GISP2 site may be indicated, rather than the higher atmospheric loading suggested by Zielinski *et al.*

Comparison of the GISP2 SO₄²⁻ record with correctly calibrated eruption dates will undoubtedly help identify possible sources of

specific sulfate peaks. In some cases, unique identification of the source eruption is possible through analyses of volcanic glass from the GISP2 core and candidate eruptions (9). Such unambiguous source identifications are important for investigating the impact (if any) of volcanism on Holocene climate.

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Response: Southon and Brown and Fiedel point out the need for conversion of the radiocarbon age of eruptions to calendar years to match to our record of volcanism (1). Southon and Brown also provide a list of calibrated-age ranges for the radiocarbon-dated volcanic eruptions between 1 and 7000 B.C. (their table 1) that we presented in table 2 of our report (1). We appreciate Southon and Brown's development of this table as they are aware of the most up-to-date calibrations used in making the conversion from radiocarbon years to calendar years. Consequently, we take this opportunity to present a revised list of the possible years of high SO₄²⁻ deposition that may be related to these eruptions (Table 1), although this is only 18 of the 232 events recorded from 1 to 7000 B.C. This table does not include the five eruptions younger than and including the Yantari eruption because the year of the SO₄²⁻ signal in our report falls within the range of calibrated ages. This also may be the case for radiocarbon-dated eruptions between A.D. 100 and 700. However, as we did stated in our report, any match between the SO₄²⁻ peaks in the GISP2 core and known volcanic eruptions must be considered tentative (2). The significance of our record is the development of a high-resolution record of the direct deposition of volcanic aerosols over the last 9000 years that is not available in any other medium. Our continued work on locating and identifying tephra in the GISP2 ice core is an important means of determining the source of the chemical signal, as was correctly cited by Southon and Brown.

Several other points raised by Southon and Brown warrant clarification. We stated in our report that the large SO₄²⁻ peaks in the early Holocene could be from either Icelandic volcanism (proximal) or Kamchatkan and Alaskan volcanism (directly upwind from Greenland), or both. Further, highly silicic eruptions from the Northern Pacific are capable of loading the atmo-

Table 1. Possible year (B.C.) of SO₄²⁻ signal in the GISP2 ice core for 18 volcanic eruptions between 1 and 7000 B.C. based on calibrated age of the eruption from Southon and Brown (7).

Eruption	Year (B.C.) of SO ₄ ²⁻ signal
Bardarbunga (Veidivotn), Iceland	1454, 1457, 1459
Aniakchak, Alaska	1623, 1669
Santorini (Minoan eruption), Greece	1623*, 1669
Long Island, New Guinea	2617
Hekla (H-4), Iceland	2310
Black Peak, Alaska	2958, 3201
Akutan, Alaska	3977
Towada, Japan	4267
Kikai, Ryuku	5277, 5279
Avachinsky, Kamchatka	5277, 5279
Masaya, Nicaragua	No appropriate signal
Mazama, Oregon	5675, 5676
Hekla (H-5), Iceland	5781
Hangar, Kamchatka	5781
Kizimin, Kamchatka	5954, 5995
Tao-Rusyr, Kurile Island	6271, 6338
Karymsky, Kamchatka	6476
Vesuvius, Italy	6955

*Our suggestion that the signal for the Santorini eruption could be 1623 B.C. was based on the similar age suggested by dendrochronological evidence. See note 32 of our report (7).

sphere with high amounts of sulfur-bearing gases because of the potential for efficient degassing and the eruption of large volumes of magma (3). Atmospheric loading estimates derived from the petrologic method may be unreliable, thus the Aniakchak eruption may not be the most likely source for the highest sulfate peak recorded in the 17th century B.C. (4).

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Delayed Helix Formation of Mutant Collagen

J. Bella *et al.* (1) demonstrate that the conformation of triple helices formed by collagen-like (Pro-Hyp-Gly)₁₀ peptides is altered when a Gly → Ala substitution is introduced in the center of each peptide, which results in a small local untwisting of the triple helix and reduced thermal stability. Bella *et al.* conclude that similar conformational changes may occur in Gly → X

mutated collagens responsible for various heritable connective tissue disorders. It has been repeatedly shown that these mutant collagen molecules exhibit decreased thermal stability, decreased collagen secretion, and increased proteolytic sensitivity (2) and—as Bella *et al.* quote—it has been suggested that this kind of mutation represents a defect in the folding of the triple helix (3).

We have demonstrated the hitherto postulated delay in the proper, zipper-like folding of collagen I in fibroblasts derived from patients with osteogenesis imperfecta (4), a heritable, generalized connective tissue disorder characterized by brittleness of bones and weakness of other tissues rich in collagen I (5). In five cell strains harboring a single Gly → Cys substitution at positions 94, 223, 526, 691, and 988 in the helical domain of the α1(I) chain, formation of full-length protease-resistant triple-helical molecules containing mutant α1(I) chains was delayed by 5 to 60 min. The delay was correlated inversely with the thermal stability of abnormal molecules. In another cell strain that harbors the mutation Gly → Cys in the COOH-terminal telopeptide just outside the helical region, folding time and melting temperature were normal. The mutations representing identical steric obstacles in the backbone of the triple helix caused different kinetic hindrance depending on their position on the molecule. Similar delays were observed with other mutations in collagens I and III (6). The observed differences in the folding delay in the Gly → Cys mutations might be, as suggested, a result of local variations in torsional flexibility which, in turn result from the appearance of particular residues in the X and Y positions (1). This sequence dependence of the triple-helical conformation will be clarified as crystal structures of other peptides containing non-Pro-Hyp-Gly triplets are determined by the approach chosen by Bella *et al.* (1).

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