THE INFLUENCE OF PRETREATMENT ON HUMIC ACID YIELD AND ^{14}C AGE OF *CAREX* PEAT

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ABSTRACT. The object of the study was to assess the effects of a range of pretreatment/extraction schemes on the yields of humic acid and humin obtained from peat and the subsequent radiocarbon ages. We analyzed peat from Flókadalur in northern Iceland, collecting material from a profile containing seven visible tephra horizons in the upper 3 m, whose form and extent indicated little disturbance to the section over the last 4000 yr. The results of a range of pretreatments demonstrated that time rather than the strength of alkali is the more important factor governing the extraction of humic acid. An increase in alkali molarity did not correspond to any systematic increase in yield, whereas an increase in time did, implying that the extraction is kinetically controlled. We found no evidence of variability in ^{14}C age due to pretreatment scheme or between different geochemical fractions of the peat. Further implications from this study are that bog stability and ecological simplicity produce a favorable environment for ^{14}C dating.

INTRODUCTION

Peat is one of the most commonly dated materials used for palaeonenvironmental reconstruction because it contains an excellent palaeoecological record that details natural and anthropogenic environmental changes (*e.g.,* pollen and plant macrofossils). It is possible, however, that anomalous ages may be inferred from ^{14}C measurements made on peat because radiocarbon dating of associated material and different physical and chemical fractions of the peat itself have been found to produce significantly different results (Dresser 1971; Olsson 1986; Shore *et al.* 1995). It is important that the reasons for these anomalies should be identified so that chronologies based on ^{14}C dating of peat can be as accurate as possible.

[14]C laboratories generally regard peat samples as comprising three operationally defined fractions that are essentially the products of the humification process, namely, 1) humic acid—the alkali soluble, acid insoluble fraction; 2) fulvic acid—the acid and alkali soluble fraction; and 3) humin—the acid and alkali insoluble fraction. In practice, the humin fraction may contain many components unrelated to humification. The commonly dated fractions are humic acid and humin, and opinions differ as to their suitability, with one of the concerns being possible humic acid mobility. It is widely accepted that fulvic acid removal is essential as this fraction is acid soluble and generally considered to be mobile (Shore *et al.* 1995). In this paper, we consider pretreatment techniques and their influence on humic acid yield and assess the implications for ^{14}C dating.

Contrasts in Pretreatment and Possible Implications for [14]C Ages

The pretreatment which peat samples undergo in order to isolate particular fractions and/or to remove potential contaminants can vary significantly between ^{14}C laboratories. One approach is to restrict pretreatment to an acid wash to remove the fulvic acid component but this could lead to incomplete fulvic extraction through protonation of the carboxylic acid groups. A different approach is to follow the acid wash with one of alkali solution, to extract the humic and fulvic acids. Acidification of the extract precipitates the humic acid, leaving the fulvic acid in solution. The humic acid fraction and/or the remaining humin fraction are then dated. Several different techniques can be used for the isolation of these fractions, ranging from a straightforward alkali/acid treatment to more elaborate schemes. In addition, concentrations of the alkali and acid and the duration of the

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extraction can also vary. It is often assumed that these factors do not affect the results but the possibility exists that pretreatment may introduce a variable bias to the dating of peat.

Williams (1989), having noted inconsistencies between stratigraphic and ^{14}C date sequences in freshwater peat, assessed the effect of alkali molarity and duration of extraction on the ^{14}C activity of the resultant humin and humic acid fractions. The results indicated that the soluble fractions (humic acid) were mainly, but not exclusively, younger than the solid fraction (effectively humin) but there was no systematic variation between the two fractions. On the basis that the solid fraction gave less variable results than the humic acid, he concluded that the former was more suitable for ^{14}C dating. Because the number of different pretreatment schemes used was extensive, only one sample was used for each pretreatment, so there were no replicate results to test for internal variability. Similarly, Hammond *et al.* (1991) concluded from their study of peats and organic silts from gley podzol environments that dates of 12 ka BP and older are contaminated by younger, more mobile carbon, such as fulvic and some humic acid fractions.

Alternatively, a case can be made for dating the alkali-soluble humic-acid fraction as this is the removal of an operationally defined acid insoluble fraction from an acidic environment. In contrast, the humin fraction is less well defined and there is greater potential for the inclusion of material which is unrelated to the initial formation of the peat, such as rootlets from later vegetation growth. This view is supported by our ^{14}C dating of peats constrained by the independent alternative dating control of isochronous horizons of volcanic ash, or tephra (Dugmore *et al.* 1995). We have analyzed peat samples of the same age but derived from different parent vegetations and formed under different geochemical and environmental conditions (Dugmore *et al.* 1995) but have no evidence of the type of variability which Williams (1989) and Hammond *et al.* (1991) have observed. There is, however, a significant and perhaps critical difference in the separation of the humic acid from humin which we employ where: 1) the peat is acid washed for a minimum of 3 h in hot molar hydrochloric acid (HCl); 2) the acid is decanted off, the sample neutralized and the peat heated to *ca.* 80°C with molar sodium hydroxide (NaOH) solution for *ca.* 3 h to extract the humic acid fraction; and 3) the humic acid solution is filtered off, acidified, heated to coagulate it and then filtered and dried.

Our concern is therefore whether any deviations from this method during routine dating might induce age anomalies. To address the problem of potential variability in age, we carried out a similar type of study to that of Williams (1989) on peat collected from Flókadalur in northern Iceland where we had dated deposits of both the Hekla 3 and Hekla 4 tephra. The object of the study was to assess the robustness of a range of pretreatment/extraction schemes with regard to the yields of humic acid and humin and the ^{14}C ages which are subsequently produced. We used a range of alkali molarities, on the basis that a pretreatment comprising a short extraction time with a low molarity might dissociate the carboxylic acid groupings on the humic acid, thereby solubilizing it, whereas a higher molarity used over a longer period might significantly change the overall organic matter structure, thereby removing a rather different fraction. Thus, the fractions which would be produced might vary in terms of chemical lability and could therefore be subject to varying degrees of movement within the peat profile.

METHODS

A block of peat, measuring *ca.* 30 × 20 × 20 cm, was broken down by hand and oven dried at 50°C. The peat was then sieved through a 1.18-mm mesh and homogenized. The vegetation within the peat comprised mainly of *Carex* and did not change throughout the block. Therefore, any changes in the yield of humic acid or ^{14}C age could not be due to vegetational or stratigraphic differences. We weighed the peat into 40-g sub-samples and treated them with 500 mL of a range of molarities of

NaOH solution (0.25 to 2M). We also varied the pretreatment time from 15 to 120 min. Following treatment with NaOH, the samples were centrifuged for 20 min at 3×10^3 rpm. The humic acid solution was decanted off and the pH adjusted to 2 by the addition of 4 M HCl. This was digested at *ca.* 80°C to coagulate the precipitate of humic acid, which was then centrifuged. The precipitate was then washed with distilled water, collected by filtration, oven dried and weighed. Figures 1 and 2 show the results. The samples were then converted to benzene and analyzed for ^{14}C according to the method of Begg (1992). Conventional ^{14}C age measurements and $\delta^{13}C$ values are presented in Tables 1 and 2.
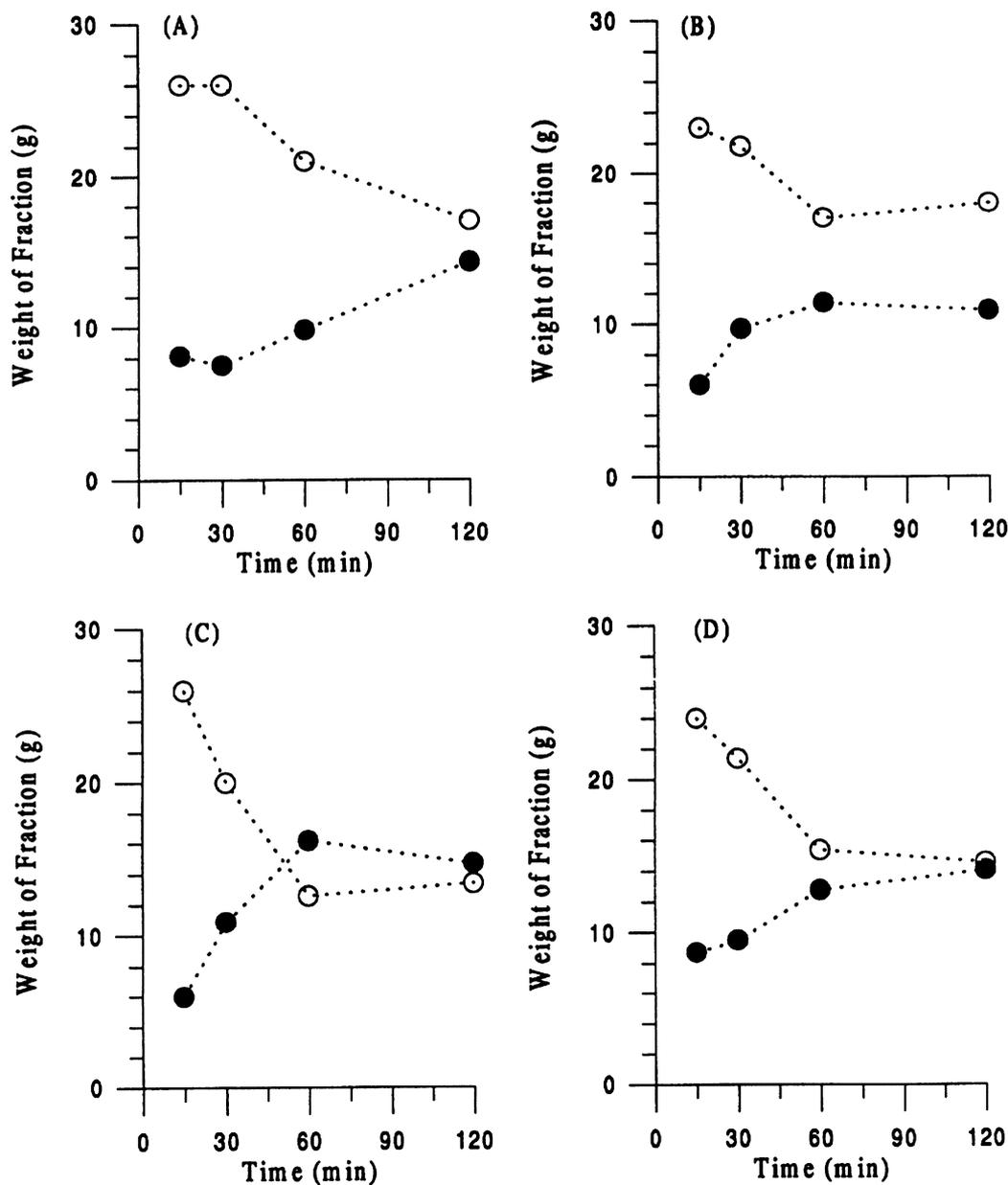

Fig. 1. Yield of humic acid versus extraction time, O = humin, ● = humic acid
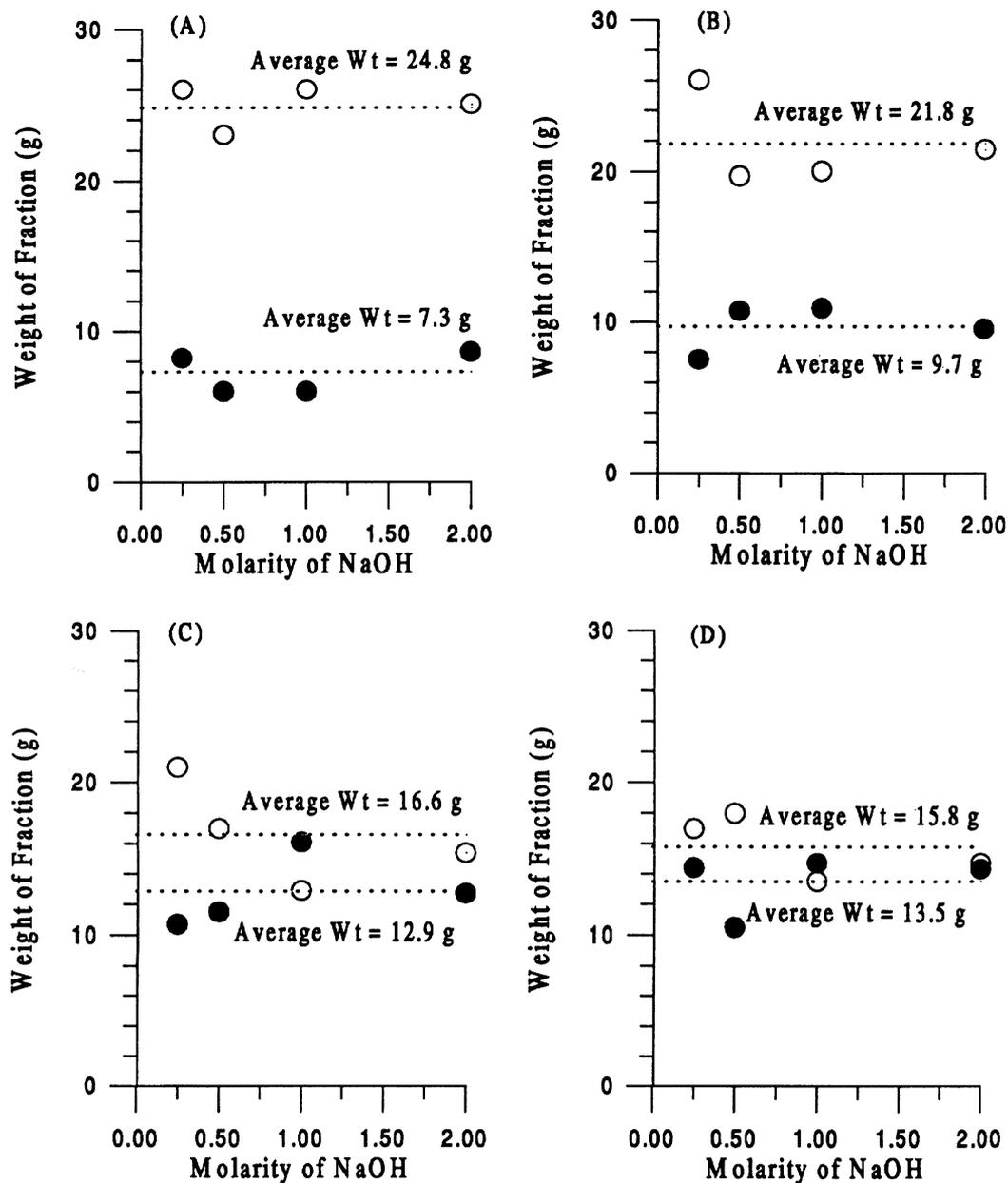
Fig. 2. Yield of humic acid versus sodium hydroxide molarity, O = humin, ● = humic acid

DISCUSSION

From Figures 1 and 2, it appears that although there are some discrepancies, time rather than the strength of alkali is the more important factor governing the extraction of humic acid. An increase in molarity does not correspond to any systematic increase in yield whereas an increase in time does. This would imply that the extraction is kinetically controlled. In general, the data indicate that, for this material at least, an extraction time of at least 1 h is required to remove a reproducible humic

acid fraction. The plots within Figure 1 do not necessarily indicate that all the humic acid has been removed; they are more likely to be saturation curves, since it can be demonstrated that successive extractions will remove more humic acid.

TABLE 1. ^{14}C Ages (yr BP ± 1σ) and δ^{13}C Measurements (‰) on Humic Acid and Humin Fractions Extracted from *Carex* Peat Using Different Pretreatment Schemes

Sample	Time (min)	NaOH (M)	HCl (M)	^{14}C Ages (humic acid)	δ^{13}C (humic acid)	^{14}C ages (humin)	δ^{13}C (humin)	^{14}C ages (whole peat)	δ^{13}C (whole peat)
1	15	0.25	4	1820 ± 50	−26.8	1850 ± 50	−28.0		
5	15	0.25	4	1670 ± 50	−29.0	1760 ± 50	−29.7		
9	15	0.25	4	1830 ± 50	−29.0	1770 ± 50	−28.3		
13	15	0.25	4	1800 ± 50	−29.0	1740 ± 50	−28.4		
2	30	0.5	4	1780 ± 50	−29.0	1830 ± 50	−27.9		
6	30	0.5	4	1670 ± 50	−29.1	1750 ± 50	−27.7		
10	30	0.5	4	1810 ± 50	−29.2	1770 ± 50	−28.4		
14	30	0.5	4	1740 ± 50	−29.0	1790 ± 50	−28.9		
3	60	1.0	4	1800 ± 50	−28.0	1770 ± 50	n/a		
7	60	1.0	4	1760 ± 50	−29.3	1720 ± 50	−28.0		
11	60	1.0	4	1810 ± 50	−29.3	1830 ± 50	−28.2		
15	60	1.0	4	1790 ± 50	−30.0	1880 ± 50	−28.2		
4	120	2.0	4	1800 ± 50	−29.0	1790 ± 50	−28.2		
8	120	2.0	4	1830 ± 50	−29.2	1750 ± 50	−28.1		
12	120	2.0	4	1900 ± 50	−30.0	1810 ± 50	−27.9		
16	120	2.0	4	1820 ± 50	−29.2	1800 ± 50	−28.7		
17	30	0.25	4	1720 ± 50	−29.1	1810 ± 50	−28.6		
18	120	0.25	4	1820 ± 50	−29.0	1850 ± 50	−28.1		
19	30	0.5	4	1800 ± 50	−29.0	1790 ± 50	−28.3		
20	120	0.5	4	1760 ± 50	−28.9	1770 ± 50	−28.0		
21	30	1.0	4	1810 ± 50	−28.0	1830 ± 50	−28.2		
22	120	1.0	4	1790 ± 50	−29.1	1820 ± 50	−27.9		
23	30	2.0	4	1790 ± 50	−29.1	1820 ± 50	−28.3		
24	120	2.0	4	1760 ± 50	−29.0	1790 ± 50	−28.1		
25	180	None	6					1740 ± 50	−28.6
26	180	None	1					1810 ± 50	−28.8

TABLE 2. Mean ^{14}C ages (yr BP ± 1σ) and δ^{13}C Measurements (‰) for Replicate Measurements on *Carex* Peat

Time (min)	NaOH molarity	Mean humic acid age	Mean δ^{13}C	Mean humin age	Mean δ^{13}C
15	0.25	1780 ± 37	−28.5	1780 ± 25	−28.6
30	0.5	1750 ± 30	−29.1	1785 ± 25	−28.2
60	1.0	1790 ± 25	−29.2	1800 ± 35	−28.1
120	2.0	1838 ± 25	−29.4	1788 ± 25	−28.2
All data		1795 ± 19	−29.1	1787 ± 13	−28.3

The results given in Tables 1 and 2 demonstrate that there are no significant differences in the age measurements made on the humic acid samples, indicating that, for this material, removal of a non-reproducible fraction of the humic acid does not affect the final age. Also, there are no differences in ^{14}C age between the humin samples, no differences in age between the humic acid and the humin frac-

tions and no differences between any of these and the age measurements made on samples which were simply acid washed (Table 1). Table 2 combines the replicate measurements which were made within this study and demonstrates that they are reproducible. The average of all the ^{14}C measurements made on the humic acid is indistinguishable from the average of the measurements made on the humin.

The robustness of the techniques that we have evaluated contrasts with the inconsistencies observed by Dresser (1971), Williams (1989) and Shore *et al.* (1995). There are several possible explanations.

Our site included seven visible tephra horizons in the upper 3 m (Fig. 3). These layers are coherent over a horizontal section of >50 m exposed by ditch digging shortly before we carried out our sam-
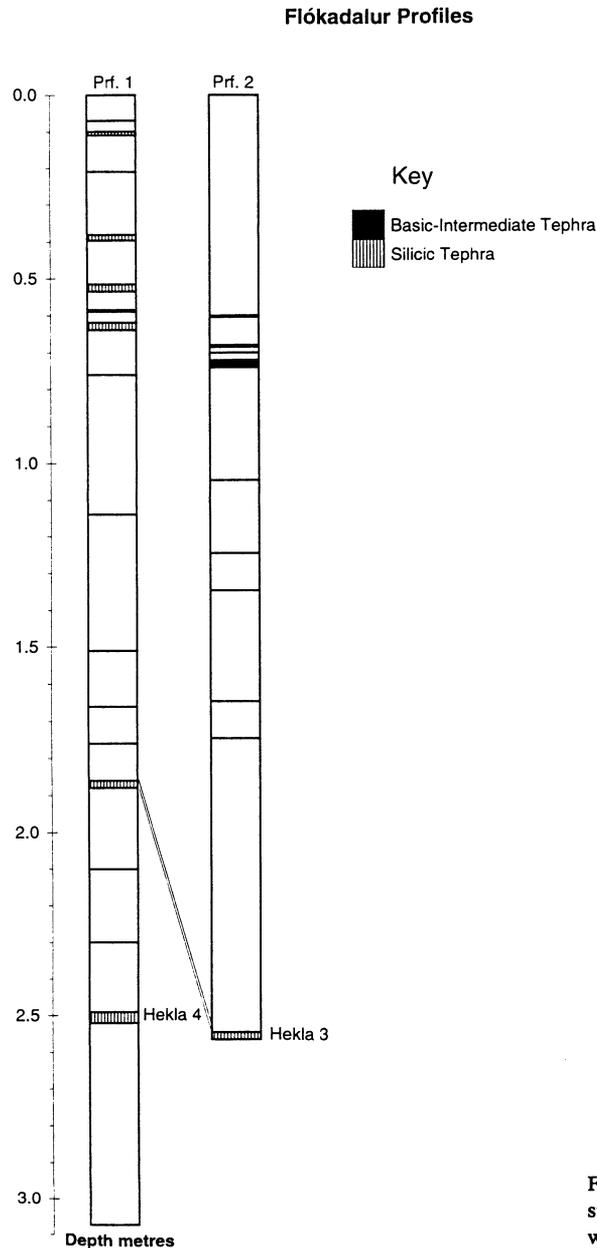
Flókadalur Profiles

Fig. 3. Flókadalur profiles. The monolith used in this study was collected from between 80 and 110 cm depth within profile 1.

pling. In the sampled section, tephra makes up <4% of the total profile, with individual horizons ranging from 0.5 to 3 cm thickness. The tephra are not of a sufficient number or scale to cause significant, long-lasting effects on bog ecology and development, and their form and extent indicates that there has been little disturbance of the sequence. Accumulation of the peat has been rapid (*ca.* 15 cm a^{-1}) and this contrasts with the profiles from northern England investigated by Shore, Bartley and Harkness (1995), where accumulation varied from >500 cm a^{-1} to <30 cm a^{-1} and where significant differences in the ^{14}C ages were identified on humic acid and humin peat fractions. The biota of the Icelandic bogs is less diverse than that of the British Isles (Löve 1983), being effectively a subset of the northwest European biota (Buckland *et al.* 1995; Steindórsson 1962) and it may be that complexity in the biota somehow contributes to these dating anomalies. Thus, rapid accumulation, bog stability and ecological simplicity may contribute to a particularly favorable environment for ^{14}C dating.

CONCLUSION

The results of this study demonstrate that ^{14}C dating of peat is not always a complex issue in which different fractions and extraction techniques produce different age measurements since, for this site, we have produced a suite of results which are entirely consistent. Selecting a site in northern Iceland has enabled us to control some variables in order to focus on the effects of pretreatment and so provide effective reference data against which other factors may be evaluated. In this instance, the site in question is of limited floral diversity and includes fine-grained narrow tephra horizons, indicating that the site is undisturbed. The implication is that elsewhere, floral diversity and/or post depositional disturbance may play a key role in generating ^{14}C age anomalies within peat. It also indicates that this type of environment is particularly suitable for ^{14}C dating and that the Icelandic source areas are one of the best places to date the tephra layers that have dispersed throughout the northeast Atlantic region (Dugmore, Larsen and Newton 1995).

ACKNOWLEDGMENTS

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