The analytical study of carbonized grain remains from the Lake Balaton region (Hungary)

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ABSTRACT. – Methods developed for the measurement of macro as well as trace elements and amino acid contents in food and feed chemistry were applied in the study of carbonized grain finds from Roman Period, Migration Period and Hungarian Late Middle Ages deposit. Even the carbonized state of archaeological grain finds posed no difficulty since this process probably took place slowly and gently. Otherwise not even traces of heat sensitive organic molecules would have survived. The macro elements identified are indicative of large molecule organic compounds. Some of these elements may have already disappeared from the deposits during the primary decomposition of organic molecules and could easily have been bleached by water. Trace elements are significantly more stable. Results of the analyses under discussion here show that the average trace element content of ancient cereals exceeded that of their modern counterparts by some 30%. The mere fact that amino acids could be identified, shows that the carbonized samples were not subjected to rapid burning. It may be assumed therefore that these remains undoubtedly underwent a gentle and slow carbonization process in an anaerobic environment.

KEY WORDS – archaeobotany, foodremain analyses, macro and trace elements, amino acid contents, carbonized grains, Cerealia, Roman Period, Migration Period and Hungarian Late Middle Ages.

MATERIAL AND METHODS

Analytical methods developed for the identification of macro as well as trace elements and amino acids in food and feed chemistry were used in the study of carbonized grain finds from the region of Lake Balaton. The material investigated included remains from the Roman Period (Keszthely - Fenékpuszta, 5th century AD), Migration Period (Fonyód - Bélatelep, 8th century) and the Hungarian Late Middle Ages (Pogányszentpéter, 16th century) (fig. 1). The procedures presented here can also be used in the evaluation of archaeobotanical grain finds. Even their carbonized state poses no difficulty. In spite of appearances they are often not entirely destroyed. Although it is possible to distinguish between slow, natural carbonization resulting from the joint effects of pressure, temperature and long exposure time (Inkohlung in German) and rapid carbonization caused by fire (charring; Verkohlung in German) archaeobotanical finds usually fall within this latter category. Otherwise their heat sensitive organic molecules would not have survived even in traces.

The series of data presented here result from attempts to draw conclusions concerning the nutritional value of carbonized grain finds recovered from Hungarian archaeological sites.

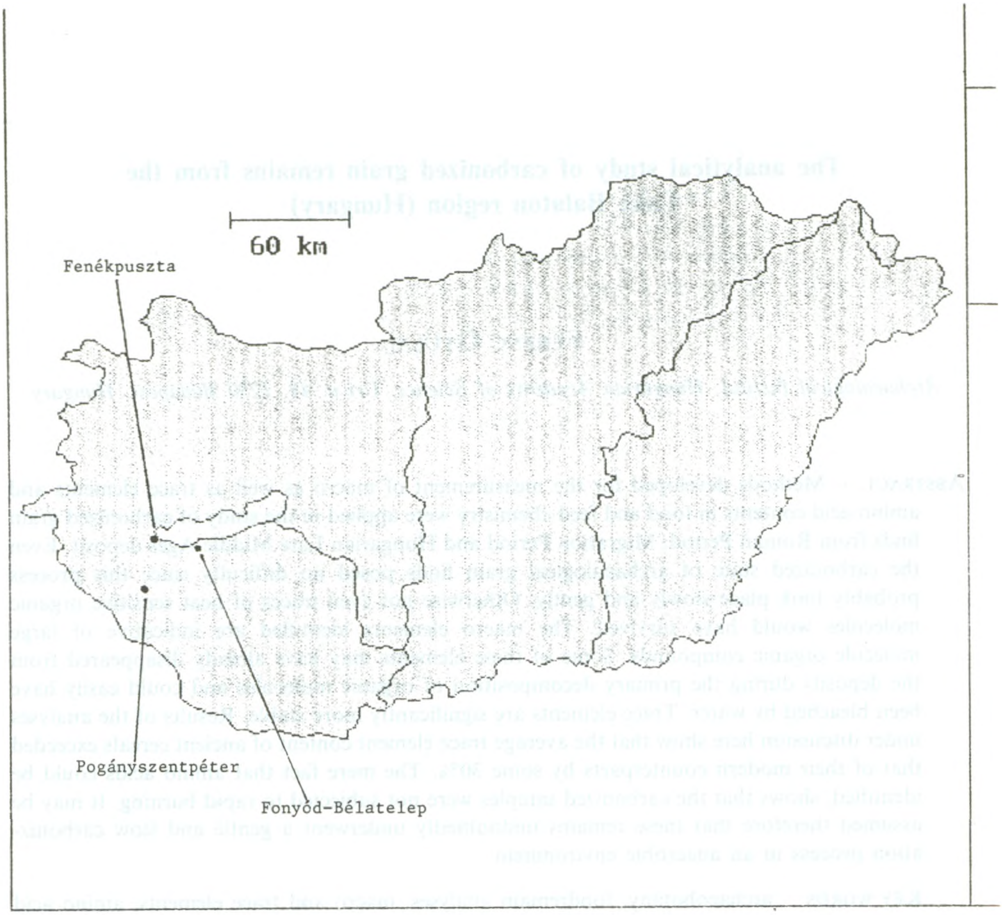

Fig. 1 – Map of the excavation sites.

The analyses were carried out in 1989 at the Central Laboratory of the Faculty of Animal Science in the Pannon Agricultural University at Kaposvár, Hungary.

For the purposes of macro element identification, the samples of carbonized grain were first ground. Subsequently, they were dried until they reached constant mass and then pulverized. Dry matter content was calculated as the resulting loss of mass. The samples prepared in this manner were treated by selenium dissolved in hot, concentrated sulphuric acid. Following this process the resulting liquid was cooled and homogenized. Plant nitrogen content transformed into ammonium sulphate during this corrosion treatment was measured by photometry at a wavelength of 630 nm with the help of a Contiflo apparatus. During the same procedure, the phosphorus content of the sample turned into orthophosphate. When exposed to ammonium metavanadate and ammonium molybdenate reagents, orthophosphate transformed into a yellow phosphorus-molybdenum-vanadium complex. The intensity of its color was also measured with the Contiflo apparatus at a wavelength of 400 nm.

The end product of sulphuric acid corrosion was used in the measurement of potassium content as well using atom emission spectrophotometry (AES; wavelength $\lambda = 700$ nm) using the same Contiflo equipment.

In order to measure the trace element content of the samples, organic plant remains were treated with concentrated chloric acid. In order to promote hydrolysis, the temperature was increased. After cooling, the solution was diluted and filtered. The resulting liquid served to evaluate the calcium, magnesium, copper, zinc and manganese content. In order to neutralize the noise created by the presence of ions, it was diluted with a solution of strontium chloride prior to analysis in the Contiflo apparatus. Atom absorption spectrophotometry (AAS) was chosen as the method of measurement (λ Ca = 700 nm, λ Mg = 285.2 nm, λ Cu = 324.7 nm, λ Zn = 213.8 nm, λ Mn = 279.5 nm).

The principle of emission flame photometry is the measurement of light intensity emitted by atoms stimulated by high temperature flame (Halász 1974). In the case of atom emission spectrophotometry (AES), the atoms and molecules to be studied are stimulated both by the flame and to a lesser extent by chemical energy. Particles, stimulated and unstable, dispose of excess energy in the form of electromagnetic radiation. The wavelength of this radiation is characteristic of each material. The intensity of radiation emitted is proportional with the number of emitting particles. Atom absorption spectrophotometry (AAS) atoms present in the flame in a basic state are stimulated by an external light source. Decrease in the intensity of this light after having passed through the flame is measured using a spectrophotometer.

Amino acid analyses were carried out under the direction of J. Csapó in 1989 at the Central Laboratory of the Faculty of Animal Science in the Pannon Agricultural University at Kaposvár, Hungary.

Samples obtained for the purposes of this study were first ground to flour quality in a Microculatti grinding mill. Raw protein content and amino acid composition were determined using the resulting grist. Raw protein content was measured using a Kjell-Foss (Foss Electric, Denmark) rapid nitrogen analyzer. Amino acid composition was determined with an LKB 4101 type (LKB Biochrom, England) automatic amino acid analyzer. The parameters for these measurements were chosen following Csapó, Tóth-Pósfai and Csapó-Kiss (1986).

The excavator archaeologists whom I got the seed samples from, could give me a guarantee that the seeds had not got into contanct with the soil at all.

The carbonized seeds under discussion here originate from storage vessels, therefore they were in no direct contact with soil or soil ingredients. Soil microbes could not affect these finds. No traces of any humic acid was identified during the course of the analysis.

It is for this reason that they may be considered intact, all the materials identified belonged to the original seeds.

The evaluation of analytical studes

The samples available for study made the analysis of chemical composition and factors of nutritional value possible in several cereal species. They also offered an opportunity for comparative studies. Since no studies of carbonized subfossil plant macro remains have been carried out previously, the verification of results presented here will require further, systematic study. In the absence of a complete series of data the scope of our observations was limited. Hopefully, however, additional analyses will be possible. Since these investigations shed light on the plant cultivation and dietary habits of past times and provide information that would not be available by any other means, it would be procedure in addition to the morphological and metric studies of plant finds from archaeological sites.

The macro elements identified are indicative of the presence of large molecule organic materials (Table 1). Some of these elements may have been lost when the remains partially decomposed. Some of the ingredients may

TABLE 1

ELEMENT CONTENTS MEASURED IN CARBONIZED GRAIN DIASPORA FINDS FROM VARIOUS ARCHAEOLOGICAL PERIODS

		Fonyód-Bélatelep 8th century Chenopodium album	Fenékpuszta 5th century Hordeum vulgare subsp. distichum	Fonyód-Bélatelep 8th century Hordeum vulgare subsp. distichum	Fonyód-Bélatelep 8th century Hordeum vulgare subsp. hexastichum	Fenékpuszta 5th century Secale cereale	Fonyód-Bélatelep 8th century Secale cereale	Pogányszentpéter 16th century Secale cereale	Fonyód-Bélatelep 8th century Panicum miliaceum
N	(%)	2,55	2,09	2,82	2,79	3,22	2,78	2,42	4,01
P	(%)	0,41	0,82	0,39	0,31	0,86	0,38	0,22	0,25
K	(%)	0,10	0,08	0,43	0,66	0,07	0,63	0,22	0,24
Na	(%)	1,46	0,18	0,27	0,26	0,04	0,25	0,31	0,12
Ca	(%)	1,134	3,044	0,879	1,839	3,648	1,722	4,510	0,934
Mg	(%)	0,331	0,816	0,103	0,323	1,385	0,389	0,792	1,197
Fe	(mg/kg)	1481	447	1350	1445	514	1735	511	1138
Mn	(mg/kg)	8,9	88,4	35,6	59,0	53,6	36,8	166,3	8,9
Zn	(mg/kg)	60,8	52,6	29,7	39,1	73,5	36,2	55,7	116,7
Cu	(mg/kg)	13,1	5,1	3,6	3,8	4,9	4,4	5,2	5,6

		Fenékpuszta 5th century Triticum monoccum	Fenékpuszta 5th century Triticum turgidum subsp. dicoccum	Fenékpuszta 5th century Triticum aestivum subsp. vulgare	Fonyód-Bélatelep 8th century Triticum aestivum subsp. vulgare	Pogányszentpéter 16th century Triticum aestivum subsp. vulgare	Fonyód-Bélatelep 8th century Triticum aestivum subsp. compactum	Pogányszentpéter 16th century Triticum aestivum subsp. compactum
N	(%)	3,84	4,26	2,76	3,74	2,74	2,74	2,63
P	(%)	0,15	0,13	0,70	0,27	0,28	0,23	0,25
K	(%)	0,09	0,01	0,10	0,68	0,06	0,07	0,3
Na	(%)	0,02	0,04	0,03	0,05	0,12	0,10	0,20
Ca	(%)	2,483	2,011	3,084	2,134	3,380	2,140	4,513
Mg	(%)	0,657	0,631	1,137	0,443	0,875	0,457	0,779
Fe	(mg/kg)	302	271	924	2370	347	1519	410
Mn	(mg/kg)	20,8	4,5	300,2	45,3	99,6	87,9	153,8
Zn	(mg/kg)	198,4	87,2	276,1	197,9	50,4	36,8	58,0
Cu	(mg/kg)	2,1	1,0	3,6	10,0	3,9	4,1	4,6

have been bleached during deposition as well. It is therefore understandable why they only appear in negligible amounts in subfossil grain finds. For the same reason, it may be said that their information content is low. On the other hand, trace elements are much more stable. These investigations reveal that the micro element content of ancient grains was significantly higher (30% as an average) than that of modern cereals (cf. Tarján and Lindner 1981). However, there were no cases in which toxically high values were measured.

Amino acid analyses yielded some unexpected results (Table 2). The mere fact that amino acids could be identified permits the conclusion that the grains were not subject to rapid burning. Charred remains would not allow the detection of amino acids and nitrogeneous compounds (raw proteins). This latter group, however, was sometimes present in high concentrations. One may therefore assume that these remains, in every case, were carbonized slowly and gently, in an anaerobic environment.

Assuming that these grains have not been sprinkled with any liquid a high nitrogen content, or were not soaked in such agents for the purposes of preservation or ground water polluted by high levels of fertilizer did not reach the deposits, it seems that during the course of 400 years some 85-90% of the amino acids in these grain remains decomposed. In the case of 1700-2000 years a 93-95% decomposition rate may be expected (Csapó, unpublished data).

The decomposition process of proteins results in the release of free amino acids and ammonium. Test results suggest that this ammonium could not escape from the bulk of the grain and was, in some form, bound to the dominant macromolecular carbohydrates. This assumption is illustrated by the high raw material content observed in our samples (Ammonium, a nitrogeneous compound, contributes to the proportion of raw protein during the measurement). As mentioned previously, the differential decomposition times of various amino acids result in diachronically changing proportions between these amino acids (Csapó, Tóth-Pósfai and Csapó-Kiss 1986).

Results expressed as grams of amino acid per 100 g grain show that the earliest samples contained the smallest amounts of amino acids. Their quantities increase in leater periods. This trend shows that the amino acid content of samples decreases with the advancement of time. If it is hypothesized that the chemical composition of samples taken from a variety of deposits changed in similar ways over centuries, the decrease in amino acid contents of grain preserved under similar conditions may be used in dating grain bearing deposits from different periods.

A graphic representation of results concerning wheat is shown in fig. 2. A number of curves may be fitted to the three points marked by the studied samples. Graphic extrapolation, however, seems to be a more feasible method of evaluation. When the intersection point between the proportion of a particular amino acid (g/100 g grain; ordinate) and its respective decomposition curve is projected onto the time scale (abscissa) an approximate date may be established directly. The ten samples studied here, however, may not yet be

TABLE 2

AMINO ACID CONTENTS MEASURED IN CARBONIZED GRAIN DIASPORA FINDS FROM VARIOUS ARCHAEOLOGICAL PERIODS

Fenékpuszta 5th century Avena sativa			Fonyód-Bélatelep 8th century Avena sativa			Fonyód-Bélatelep 8th century Chenopodium album		
asp	0.033	10.03	asp	0.085	9.5505	asp	0.354	10.427
tre	0.015	4.5592	tre	0.033	3.7078	tre	0.174	5.1251
ser	0.012	3.6474	ser	0.032	3.5955	ser	0.195	5.7437
glu	0.03	9.1185	glu	0.107	12.022	glu	0.309	9.1016
pro	0.012	3.6474	pro	0.064	7.191	pro	0.212	6.2444
gli	0.027	8.2066	gli	0.063	7.0786	gli	0.441	12.989
ala	0.015	4.5592	ala	0.061	6.8539	ala	0.231	6.8041
cis	0.003	0.9118	cis	0.014	1.573	cis	0.008	0.2356
val	0.009	2.7355	val	0.053	5.955	val	0.238	7.0103
met	0.009	2.7355	met	0.017	1.9101	met	0.044	1.296
iso	0.015	4.5592	iso	0.024	2.6966	iso	0.12	3.5346
leu	0.009	2.7355	leu	0.058	6.5168	leu	0.223	6.5684
tir	0.038	11.55	tir	0.134	15.056	tir	0.365	10.751
pha	0.024	7.2948	pha	0.062	6.9662	pha	0.178	5.243
lys	0.033	10.03	lys	0.051	5.7303	lys	0.106	3.1222
hys	0.018	5.4711	hys	0.01	1.1236	hys	0.073	2.1502
arg	0.027	8.2066	arg	0.022	2.4719	arg	0.124	3.6524
tri	—	—	tri	—	—	tri	—	—
	0.329			0.89			3.395	

Fenékpuszta 5th century Hordeum vulgare subsp. distichum cv. nudum			Fonyód-Bélatelep 8th century Hordeum vulgare subsp. distichum cv. nudum			Fonyód-Bélatelep 8th century Triticum aestivum subsp. vulgare		
asp	0.052	11.158	asp	0.083	10.323	asp	0.064	11.169
tre	0.021	4.5064	tre	0.034	4.2288	tre	0.027	4.712
ser	0.022	4.721	ser	0.028	3.4825	ser	0.023	4.0139
glu	0.054	11.588	glu	0.098	12.189	glu	0.076	13.263
pro	0.039	8.3691	pro	0.062	7.7114	pro	0.037	6.4572
gli	0.036	7.7253	gli	0.062	7.7114	gli	0.048	8.3769
ala	0.032	6.8669	ala	0.053	6.592	ala	0.035	6.1082
cis	0.003	0.6437	cis	0.013	1.6169	cis	0.005	0.8726
val	0.029	6.2231	val	0.052	6.4676	val	0.034	5.9336
met	0.005	1.0729	met	0.01	1.2437	met	0.011	1.9197
iso	0.018	3.8626	iso	0.029	3.6069	iso	0.024	4.1884
leu	0.033	7.0815	leu	0.068	8.4577	leu	0.043	7.5043
tir	0.033	7.0815	tir	0.049	6.0945	tir	0.036	6.2827
pha	0.041	8.7982	pha	0.088	10.945	pha	0.037	6.4572
lys	0.028	6.0085	lys	0.044	5.4726	lys	0.035	6.1082
hys	0.006	1.2875	hys	0.01	1.2437	hys	0.007	1.2216
arg	0.014	3.0042	arg	0.021	2.6119	arg	0.031	5.4101
tri	—	—	tri	—	—	tri	—	—
	0.466			0.804			0.573	

TABLE 2 (concluded)

AMINO ACID CONTENTS MEASURED IN CARBONIZED GRAIN DIASPORA FINDS FROM VARIOUS ARCHAEOLOGICAL PERIODS

Pogányszentpéter 16th century Triticum aestivum subsp. vulgare			Fenékpuszta 5th century Triticum aestivum subsp. vulgare			Fonyód-Bélatelep 8th century Triticum aestivum subsp. compactum		
asp	0.179	11.215	asp	0.045	11.842	asp	0.074	10.898
tre	0.062	3.8847	tre	0.024	6.3157	tre	0.029	4.2709
ser	0.07	4.3859	ser	0.024	6.3157	ser	0.026	3.8291
glu	0.214	13.408	glu	0.047	12.368	glu	0.067	9.8674
pro	0.109	6.8295	pro	0.018	4.7368	pro	0.032	4.7128
gli	0.014	8.7719	gli	0.031	8.1578	gli	0.061	8.9838
ala	0.078	4.8872	ala	0.022	5.7894	ala	0.049	7.2164
cis	0.016	1.0025	cis	0.004	1.0526	cis	0.006	0.8836
val	0.082	5.1378	val	0.018	4.7368	val	0.039	5.7437
met	0.029	1.817	met	0.007	1.8421	met	0.015	2.2091
iso	0.086	5.3884	iso	0.014	3.6842	iso	0.034	5.0073
leu	0.109	6.8295	leu	0.025	6.5789	leu	0.055	8.1001
tir	0.094	5.8897	tir	0.023	6.0526	tir	0.051	7.511
pha	0.101	6.3283	pha	0.024	6.3157	pha	0.053	7.8056
lys	0.103	6.4536	lys	0.024	6.3157	lys	0.04	5.891
hys	0.023	1.4411	hys	0.008	2.1052	hys	0.016	2.3564
arg	0.101	6.3283	arg	0.022	5.7894	arg	0.032	4.7128
tri	—	—	tri	—	—	tri	—	—
	1.596			0.38			0.679	

Pogányszentpéter 16th century Triticum aestivum subsp. compactum			Fonyód-Bélatelep 8th century Hordeum vulgare subsp. distichum			Fonyód-Bélatelep 8th century Panicum miliaceum		
asp	0.181	12.388	asp	0.078	11.127	asp	0.095	12.45
tre	0.063	4.3121	tre	0.037	5.2781	tre	0.044	5.7667
ser	0.071	4.8596	ser	0.031	4.4222	ser	0.038	4.9803
glu	0.126	8.6242	glu	0.081	11.554	glu	0.074	9.6985
pro	0.063	4.3121	pro	0.039	5.5634	pro	0.03	3.9318
gli	0.142	9.7193	gli	0.052	7.4179	gli	0.057	7.4705
ala	0.095	6.5024	ala	0.03	4.2796	ala	0.065	8.519
cis	0.016	1.0951	cis	0.011	1.5691	cis	0.005	0.6553
val	0.071	4.8596	val	0.044	6.2767	val	0.043	5.6356
met	0.032	2.1902	met	0.017	2.4251	met	0.013	1.7038
iso	0.08	5.4757	iso	0.026	3.7089	iso	0.029	3.8007
leu	0.102	6.9815	leu	0.044	6.2767	leu	0.054	7.0773
tir	0.102	6.9815	tir	0.058	8.2738	tir	0.069	9.0432
pha	0.11	7.529	pha	0.079	11.269	pha	0.075	9.8296
lys	0.089	6.0917	lys	0.036	5.1355	lys	0.032	4.1939
hys	0.032	2.1902	hys	0.01	1.4265	hys	0.012	1.5727
arg	0.086	5.8863	arg	0.028	3.9942	arg	0.028	3.6697
tri	—	—	tri	—	—	tri	—	—
	1.461			0.701			0.763	

TABLE 2 (continued)

AMINO ACID CONTENTS MEASURED IN CARBONIZED GRAIN DIASPORA FINDS FROM VARIOUS ARCHAEOLOGICAL PERIODS

	Fenékpuszta 5th century Secale cereale			Fonyód-Bélatelep 8th century Secale cereale			Pogányszentpéter 16th century Secale cereale	
asp	0.04	11.204	asp	0.077	11.492	asp	0.169	11.951
tre	0.017	4.7619	tre	0.034	5.0746	tre	0.083	5.8698
ser	0.019	5.3221	ser	0.03	4.4776	ser	0.07	4.0950
glu	0.035	9.8039	glu	0.08	11.94	glu	0.14	9.9009
pro	0.019	5.3221	pro	0.042	6.2686	pro	0.068	4.809
gli	0.032	8.9635	gli	0.049	7.3134	gli	0.116	8.2036
ala	0.021	5.8823	ala	0.043	6.4179	ala	0.081	5.7284
cis	0.004	1.1204	cis	0.006	0.8955	cis	0.017	1.2022
val	0.021	5.8823	val	0.042	6.2686	val	0.079	5.5869
met	0.007	1.9607	met	0.011	1.6417	met	0.017	1.2022
iso	0.013	3.6414	iso	0.022	3.2835	iso	0.048	3.3946
leu	0.021	5.8823	leu	0.053	7.9104	leu	0.082	5.7991
tir	0.024	6.7226	tir	0.045	6.7164	tir	0.105	7.4257
pha	0.035	9.8039	pha	0.06	8.9552	pha	0.157	11.103
lys	0.024	6.7226	lys	0.034	5.0746	lys	0.095	6.7185
hys	0.005	1.4005	hys	0.009	1.3432	hys	0.017	1.2022
arg	0.02	5.6022	arg	0.033	4.9253	arg	0.07	4.9505
tri	—	—	tri	—	—	tri	—	—
	0.357			0.67			1.414	

	Fenékpuszta 5th century Triticum monococcum			Fenékpuszta 5th century Triticum turgidum subsp. dicoccum	
asp	0.045	12.064	asp	0.051	12.718
tre	0.018	4.8257	tre	0.018	4.4887
ser	0.018	4.8257	ser	0.024	5.985
glu	0.048	12.868	glu	0.051	12.718
pro	0.024	6.4343	pro	0.021	5.2369
gli	0.036	9.6514	gli	0.033	8.2294
ala	0.021	5.63	ala	0.027	6.7331
cis	0.006	1.6085	cis	0.006	1.4962
val	0.018	4.8257	val	0.017	4.2394
met	0.007	1.8766	met	0.007	1.7456
iso	0.013	3.4852	iso	0.011	2.7431
leu	0.033	8.8471	leu	0.023	5.7356
tir	0.027	7.2386	tir	0.027	6.7331
pha	0.019	5.0938	pha	0.031	7.7306
lys	0.016	4.2895	lys	0.027	6.7331
hys	0.009	2.4128	hys	0.009	2.2443
arg	0.015	4.0214	arg	0.018	4.4887
tri	—	—	tri	—	—
	0.373			0.401	

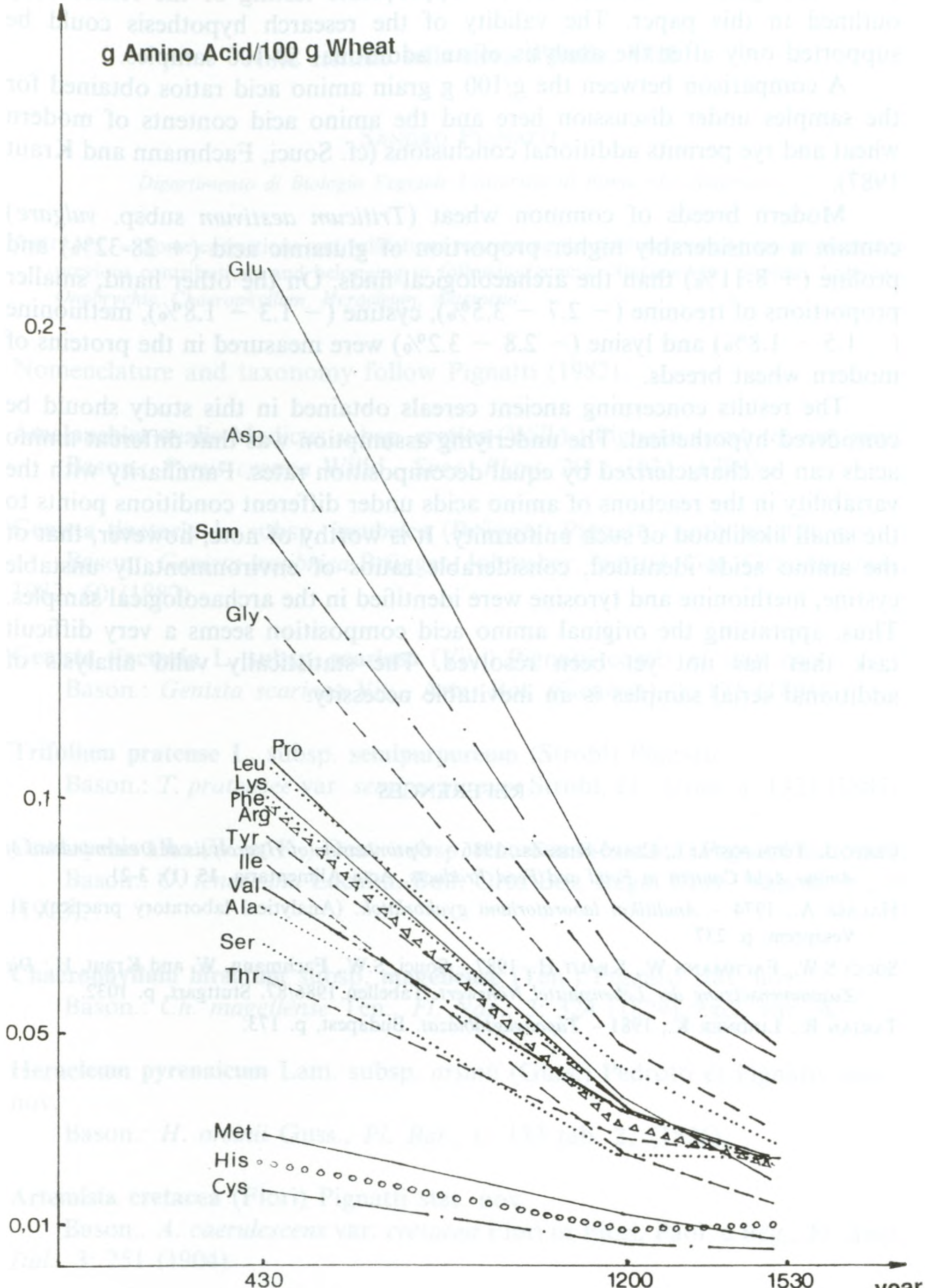

Fig. 2 – Changes in the Amino Acid Composition of Wheat (*Triticum aestivum* subsp. *vulgare*).

sufficiently great in number for the appropriate testing of the relationship outlined in this paper. The validity of the research hypothesis could be supported only after the analysis of an additional 50-100 samples.

A comparison between the g/100 g grain amino acid ratios obtained for the samples under discussion here and the amino acid contents of modern wheat and rye permits additional conclusions (cf. Souci, Fachmann and Kraut 1987).

Modern breeds of common wheat (*Triticum aestivum* subsp. *vulgare*) contain a considerably higher proportion of glutamic acid (+ 28-32%) and proline (+ 8-11%) than the archaeological finds. On the other hand, smaller proportions of treonine (− 2.7 − 3.5%), cystine (− 1.3 − 1.8%), methionine (− 1.5 − 1.8%) and lysine (− 2.8 − 3.2%) were measured in the proteins of modern wheat breeds.

The results concerning ancient cereals obtained in this study should be considered hypothetical. The underlying assumption was that different amino acids can be characterized by equal decomposition rates. Familiarity with the variability in the reactions of amino acids under different conditions points to the small likelihood of such uniformity. It is worthy of note, however, that of the amino acids identified, considerable ratios of environmentally unstable cystine, methionine and tyrosine were identified in the archaeological samples. Thus, appraising the original amino acid composition seems a very difficult task that has not yet been resolved. The statistically valid analysis of additional serial samples is an inevitable necessity.

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