

**LABORATORY OF COSMOCHEMISTRY
RADIOCARBON MEASUREMENTS I**

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The ^{14}C dates listed in this report on archaeological and geologic samples were obtained mainly from 1969 to 1974. Pretreatment of wood charcoal and carbonized fossil soil by boiling in acid, alkali, and acid, again, is standard procedure. The method employed is liquid scintillation counting of synthesized benzene using the basic techniques described by Arslanov and Gromova (1968) converting sample $\rightarrow \text{Li}_2\text{C}_2 \rightarrow \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_6$ with an overall yield to ca 90%. A vanadium-alumina catalyst is used at reduced temperature for the acetylene to benzene conversion. Anthracite coal was used for the dead carbon run.

Within the experimental error a one-to-one correlation between the activity of background and that of anthracite coal was obtained on two different runs. Several months of analyzing standards, backgrounds, and samples of known age reveal a high degree of precision and reliability in all systems (Alexeev *et al.*, 1975). All measurements of ^{14}C activity of synthesized benzene were made on a liquid scintillation counter. The scintillator vial was viewed by two photomultipliers working in coincidence. The background counting rate was reduced by massive screening and by pulse-height selection. The counter is shielded by 20 to 30cm of selected iron, 10 to 15cm paraffin wax containing 25% boric acid, 10cm stainless steel, and 2.5cm mercury. The total weight is ca 50 tons (2 secs). Table I gives the pertinent information for the counter.

TABLE I

Volume of the counting vial, ml	Background B, cpm	Modern carbon A, cpm	Fig of merit A/\sqrt{B}
5.5	3.98 ± 0.02	33.11 ± 0.04	16.6
13.6	5.2 ± 0.5	87 ± 2	38.5
27.1	9.17 ± 0.03	180.0 ± 0.3	59.5
56	14.5 ± 0.5	314 ± 3	82.5

All samples were measured at least twice, with an interval of up to one month between them. Dates are reported in conventional radiocarbon years, using the 5570 half-life, with 1950 as the reference year. The modern reference standard is 95% of the measured activity of the NBS oxalic acid standard. Age limits quoted are derived from 1σ counting statistics of background, modern, and sample counts.

$\delta^{13}\text{C}$ measurements are made on CO_2 produced in charcoal or synthesized benzene combustion, and results are given relative to the PDB

standard. The present-day value of Δ for each sample was calculated from the measured isotopic ratios using Broecker's formula (Broecker and Olson, 1961):

$$\Delta = \delta^{14}\text{C} - (2\delta^{13}\text{C} + 50)(1 + 0.001 \delta^{14}\text{C})$$

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I. ARCHAEOLOGIC SAMPLES

Ukrainian series

Wood from ancient tombs, Ukrainian SSR, USSR, coll and subm 1971 by V P Zolotun, A D Tsuryupa Agric Inst, Kherson, Ukrainian SSR.

CSM-67. Ukrainian 1 **4220 ± 50**

Wood from depth 300cm, Tomb 1, 10km W of town Novaya Odessa of the Nikolaevskaya prov. Estimated age: 2600 to 2300 BC. Tripolskaya culture.

CSM-68. Ukrainian 2 **2730 ± 40**

Wood from depth 70cm, Tomb 4. Estimated age: 1000 to 800 BC. Kemmerijskaya culture.

CSM-69. Ukrainian 3 **2850 ± 40**

Wood from depth 250cm, Tomb 31 near village Borisivka, Odessa prov. Estimated age: 1150 to 850 BC. Culture of corpses burn.

CSM-70. Ukrainian 4 **4150 ± 50**

Wood from Tomb 10, near village Majaki, Odessa prov. Estimated age is ca 2200 BC. Usatovskaya culture.

CSM-71. Ukrainian 5 **2740 ± 40**

Wood from depth 350cm, Tomb 6 near village Tatarbunary, Odessa prov. Estimated age: 1200 to 1000 BC. Srubnaya culture.

CSM-72. Ukrainian 6 **4390 ± 60**

Wood from Tomb 27 near village Lyubimovka, Kherson prov. Estimated age: 2800 to 2500 BC.

II. GEOLOGIC SAMPLES

Siberian series

Samples are from a 14m terrace of R Irkineeva, tributary of R Angara, near village Bedoba, RSFSR, USSR. Coll and subm 1969 by S A Laukhin, All-Union Scientific-Research Inst Min Prod, Moscow, USSR.

CSM-10. Siberian 1	37,950 ± 1150
Wood, 6m below terrace surface.	
CSM-11. Siberian 2	41,600 ± 1300
Wood, 8m below terrace surface.	
CSM-42. Siberian 3	42,750 ± 600
Wood, 8.5m below terrace surface. No pretreatment.	
CSM-41. Siberian 4	47,000 ± 1000
Wood from same location as CSM-42. Sample was pretreated by boiling with 5% HCl for 20 min, boiling with 2% NaOH for 12 hr with extracted humic acids, boiling with 5% HCl for 30 min. Between the stages the sample was washed with distilled water.	
CSM-43. Siberian 5	38,300 ± 1000
Humic acids extracted during pretreatment of sample CSM-41.	

Onikotan Island series

Samples from Onikotan I near near Krinitsyno volcano, Kuril Is, USSR. Coll and subm 1969 by L D Sulerzhitsky, Inst Geol, Acad Sci USSR.

CSM-438(g)-I. Onikotan I. 1-1, 31 to 40 yr	7650 ± 70
Completely carbonized tree trunk with a well pronounced trunk surface (bark has been preserved). Tree age is ca 40 yr. It died during eruption of Krinitsyno volcano. Layer of eruptive rocks is ca 40m over sampling site. Four groups of tree rings, ca 10 yr each, were prepared. CSM-438(g)-I was the group of outer tree rings, the last ca 10 yr of tree growth.	
CSM-438(g)-II. Onikotan I. 1-2, 21 to 30 yr	7750 ± 90
CSM-438(g)-III. Onikotan I. 1-3, 11 to 20 yr	7500 ± 80
CSM-438(g)-IV. Onikotan I. 1-4, 1 to 10 yr	7700 ± 110
CSM-439(g). Onikotan I. 2	7950 ± 70
Carbonized fossil soil, 20cm below CSM-438(g)-I.	
CSM-440(g). Onikotan I. 3	8230 ± 90
Carbonized fossil soil, 40cm below CSM-438(g)-I.	
CSM-440(g)-G. Onikotan I. 4	8480 ± 50
Humic acids from sample CSM-440(g).	
CSM-442(g)-I. Onikotan I. 5-1, 21 to 25 yr	9430 ± 70
Tree trunk, 2m below CSM-438(g)-I. The tree died in a mud-ash flow. Five groups of tree rings, at 5 yr each, were prepared. CSM-442(g)-I was group of outer tree rings.	

CSM-442(g)-II. Onikotan I. 5-2, 16 to 20 yr	9770 ± 100
CSM-442(g)-III. Onikotan I. 5-3, 11 to 15 yr	9280 ± 60
CSM-442(g)-IV. Onikotan I. 5-4, 6 to 10 yr	9800 ± 140
CSM-442(g)-V. Onikotan I. 5-5, 1 to 5 yr	9330 ± 120
CSM-443(g). Onikotan I. 6	24,500 ± 740

Carbonized soil at base of a thick stratum, ca 30m, of pumices formed by eruption of Nemo volcano.

Simushir Island series

Recent wood from foot of N slope of Uratman volcano, Simushir I., Kuril Is, USSR. Coll and subm 1969 by L D Sulerzhitsky, Inst Geol, Acad Sci USSR.

CSM-453(g). Simushir I. 1, +20m	$\delta^{14}\text{C} = 17 \pm 4\%$
CSM-454(g). Simushir I. 2, +40m	$\delta^{14}\text{C} = -41 \pm 4\%$
CSM-455(g). Simushir I. 3, +100m	$\delta^{14}\text{C} = -34 \pm 4\%$

Kamchatka Peninsula series

Tree rings, alder, near Kozyrevsk village, Kamchatka R, Kamchatka peninsula, USSR. The tree was cut in 1967. Coll and subm 1969 by L D Sulerzhitsky, Inst Geol, Acad Sci USSR.

CSM-452(g)-O. Kamchatka Peninsula 1	$\delta^{14}\text{C} = 382 \pm 6\%$
Tree rings, grown 1948 to 1967.	
CSM-452(g)-A. Kamchatka Peninsula 2	$\delta^{14}\text{C} = -37 \pm 5\%$
Tree rings, grown 1943 to 1947.	
CSM-452(g)-B. Kamchatka Peninsula 3	$\delta^{14}\text{C} = -48 \pm 5\%$
Tree rings, grown 1938 to 1942.	

TABLE 2
 $\delta^{13}\text{C}$ values

Lab no.	Year*	Sample	$\delta^{13}\text{C}$, ‰ ($\pm 0.4\%$)
CSM-46	1905	Charcoal	-26.2
CSM-46	1905	Benzene	-26.1
CSM-52	1908	Benzene	-24.4
CSM-55	1910-1911	Benzene	-25.9
CSM-61	1913-1914	Benzene	-26.2
CSM-65	1915-1916	Benzene	-26.4
Average			-25.9 ± 0.6

* Single yr correspond to spring-summer parts of rings, double yr to autumn-winter parts.

TABLE 3
 Δ data of sequoia tree rings

Lab no.	Year*	$\Delta \pm \delta\Delta, \%$
CSM-81	1890	18 \pm 6
CSM-82	1890-1891	13 \pm 6
CSM-83	1891	12 \pm 3
CSM-84	1891-1892	14 \pm 3
CSM-85	1892	13 \pm 3
CSM-86	1892-1893	32 \pm 4
CSM-87	1893	5 \pm 6
CSM-88	1893-1894	8 \pm 7
CSM-89	1894	27 \pm 4
CSM-90	1894-1895	21 \pm 3
CSM-91	1895	36 \pm 4
CSM-92	1895-1896	26 \pm 6
CSM-93	1896	19 \pm 3
CSM-94	1896-1897	27 \pm 7
CSM-95	1897	19 \pm 3
CSM-96	1897-1898	23 \pm 3
CSM-97	1898	27 \pm 3
CSM-98	1898-1899	19 \pm 3
CSM-99	1899	14 \pm 8
CSM-100	1899-1900	18 \pm 4
CSM-101	1900-1901	27 \pm 4
CSM-102	1901	16 \pm 3
CSM-103	1901-1902	22 \pm 3
CSM-104	1902	19 \pm 3
CSM-105	1902-1903	24 \pm 3
CSM-106	1903	16 \pm 3
CSM-107	1903-1904	19 \pm 3
CSM-108	1904	24 \pm 5
CSM-45	1904-1905	15 \pm 3
CSM-46	1905	15 \pm 3
CSM-47	1905-1906	16 \pm 4
CSM-48	1906	30 \pm 3
CSM-49	1906-1907	25 \pm 5
CSM-50	1907	30 \pm 6
CSM-51	1907-1908	19 \pm 4
CSM-52	1908	22 \pm 5
CSM-53	1908-1909	30 \pm 3
CSM-54	1909-1910	-5 \pm 4
CSM-55	1910-1911	14 \pm 3
CSM-56	1911	12 \pm 3
CSM-57	1911-1912	19 \pm 6

TABLE 3 (continued)

Lab no.	Year*	$\Delta \pm \delta\Delta, \text{‰}$
CSM-58	1912	16 ± 4
CSM-59	1912-1913	5 ± 3
CSM-60	1913	2 ± 3
CSM-61	1913-1914	15 ± 3
CSM-62	1914	2 ± 3
CSM-63	1914-1915	-41 ± 4
CSM-64	1915	4 ± 3
CSM-65	1915-1916	-2 ± 5

* See Table 2.

CSM-452(g)-C. Kamchatka Peninsula 4 $\delta^{13}\text{C} = -47 \pm 8\text{‰}$
Tree rings, grown 1933 to 1937.

CSM-452(g)-D. Kamchatka Peninsula 5 $\delta^{13}\text{C} = -41 \pm 5\text{‰}$
Tree rings, grown 1928 to 1932.

CSM-452(g)-E. Kamchatka Peninsula 6 $\delta^{13}\text{C} = -47 \pm 6\text{‰}$
Tree rings, grown 1923 to 1927.

CSM-452(g)-F. Kamchatka Peninsula 7 $\delta^{13}\text{C} = -27 \pm 6\text{‰}$
Tree rings, grown before 1923.

Sequoia tree rings series

Wood (sequoia) from Nikitsk Bot garden, Yalta, Crimea, USSR. Tree, ca 100 yr old, felled in 1964. Coll and subm 1971 by L D Sulerzhitsky, Inst Geol, Acad Sci USSR. Subsequently dendro-dated by LDS. The ^{14}C content was determined both in spring-summer and in autumn-winter parts of each tree ring. $\delta^{13}\text{C}$ was determined for some samples by E M Galimov, I M Gubkin Inst Oil-Chemical & Gas Industry, Moscow, USSR (present address: V I Vernadsky Inst Geochem & Analytical Chem USSR Acad Sci, Moscow, USSR). $\delta^{13}\text{C}$ data are shown in Table 2.

These $\delta^{13}\text{C}$ values were used for determination of Δ values of the same samples. The average value of the $\delta^{13}\text{C}$ ($-25.9 \pm 0.6\text{‰}$) was used to determine Δ values of other samples. Δ data are shown in Table 3.

A positive correlation between ^{14}C contents and no. of sunspots was found (fig 1). Correlation coefficient $+0.57 \pm 0.12$ was obtained with phase shift ca 1.7 yr, which corresponds to reliability of conclusion about positive correlation by $> 99\%$. Obtained data discussed in detail previously (Alexeev *et al*, 1975; Lavrukhina *et al*, 1973).

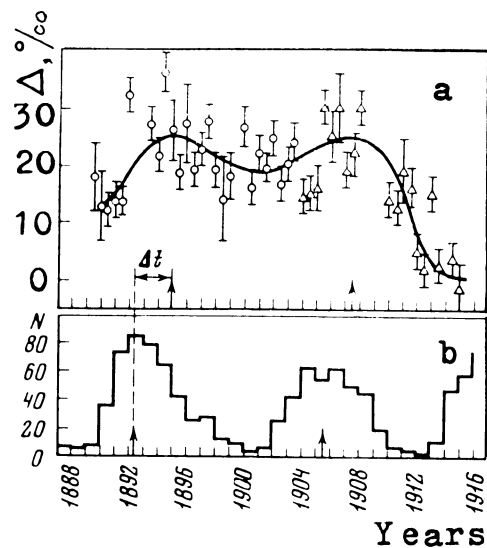


Fig. 1. Time variations of the ^{14}C content (a) and of sunspot numbers (b). The maxima are shown by arrows. The Δt is ca 1.7 yr.

REFERENCES

- Alexeev, V A, Lavrukina, A K, and Milnikova, Z K, 1975, Variations of radiocarbon content in annual rings of the sequoia (1890-1916): *Geokhimiya*, no. 5, p 667-675.
- Arslanov, Kh A and Gromova, L I, 1968, Cyclic trimerization of acetylene and alkylacetylene on the chromalumosilicate catalyzer: *Doklady Akad Nauk SSSR*, v 183, p 881-884.
- Broecker, W S and Olson, E A, 1961, Lamont radiocarbon measurements VIII: Radiocarbon, v 3, p 176-204.
- Lavrukina, A K, Alexeev, V A, Galimov, E M, and Sulerzhitsky, L D, 1973, Radiocarbon in the rings of sequoia: *Doklady Akad Nauk SSSR*, v 210, p 941-943.