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Radon and Thoron Emanation Measurements and the Effect of Ground Water

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(Abstract)

MASTER

In the past, corrections for annual dose rate calculations have used a qualitative approach to the effect of ground water saturation and radon and thoron loss. We will present an example of how this correction can now be precisely determined using natural gamma-ray activities to determine the amount of emanation from ceramic sherds and soil, both in a dry state <u>and</u> saturated with ground water. The experimental data also provide information concerning disequilibria in Th-234 and Ra-226 regions of the decay series. Additionally, approximate values of uranium and thorium concentrations (sufficiently accurate for authenticity work) are provided.

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In the past, corrections for annual dose rate calculation have used a qualitative approach to the effect of ground water saturation with radon and/or thoron loss (Zimmerman, 1971). An early report (Desai and Aitken, 1974) presented qualitative results indicating that wet conditions do not drastically inhibit the escape of radon for a diverse selection of sherds.

Improving upon a radon loss method first reported 2½ years ago (Carriveau & Harbottle, 1979), we now report an example of how this ground water correction can be accurately determined. Through measurement of natural gamma-ray activities we precisely determine the amount of emanation from ceramic sherds, powder or soil, both in a wet and dry condition.

The improvements are in three areas: reduced sample size, improved signal to background ratio through shielding, and experimental simplification by elimination of a vacuum pump. In addition, the scope of the measurements has been broadened, as suggested at the previous Specialist Seminar on TL Dating (Carriveau, Troka & Harbottle, 1978). These include: measurement of additional departures from secular equilibrium (other than emanation) and determination of uranium and thorium concentrations in samples under study for authentication purposes. Note that the experimental apparatus consists of relatively low cost instruments, normally found in most physics or chemistry laboratories.

We have felt that the use of natural gamma-ray activity to measure emanation (Carriveau & Harbottle, 1979) provides many advantages over the more commonly used alpha-counting technique (Aitken, 1978; Murray, 1980). A Ge(Li) detector was used, having a nominal volume of 30 cc with an efficiency of 12%; energy resolution requirements are very modest as the gamma-ray transitions are well separated. The sample under study, of the order of 50-100 grams, is held in a sealable glass cell of 70 cc volume (7 cm diameter x 1.8 cm thickness) and shielded by 4.5 cm thick lead.

Table 1 lists the gamma-ray transitions seen in a typical case. We have measured the activities under two conditions: either where radon and thoron loss is enhanced by a flow of gas to carry off emanation or restricted by sealing the system. This present scheme simplifies the previous apparatus (Carriveau & Harbottle, 1979) through substitution of flowing gas for the vacuum, permitting removal of the vacuum pump.

Results from an emanating material (sherds from Hong Kong) are shown in Figure 1. Activities from transitions noted by an asterisk in Table 1 are plotted and a build-up with time is seen in the post-radon and thoron daughter products when the system is sealed. An increase of 75% in the Pb-214 and Bi-214 activities and 9% in the Bi-212 and Tl-208 occurs after sealing. It is not necessary to measure as many points as shown in this figure to determine the build-up; constant values occur after two days for post thoron and fifteen days for post-radon.

From measurements of this type it is now possible to accurately measure the amount of emanation in the dry state. In fact, however, sherds are normally in some fraction of total water saturation, dependent on the rainfall and ground water level of the site. One may now introduce water to the sherds (Carriveau & Burt, 1979) and remeasure the effect of ground water uptake on the emanation. Figure 2 shows the results for the same Hong Kong sherds in their water-saturated condition (11.7% water uptake by weight). Note that the amount of post-radon and post-thoron build-up is diminished. The thoron emanation is reduced to zero and the radon loss is reduced by a factor of 0.8. Through measurements of this type one may now determine precisely the effect of ground water and make quantitative corrections to the annual dose rate calculation to produce the most accurate date determination.

The data in Table 1 may also be used to study departures from secular equilibrium <u>other</u> than those due to escape of emanation. Note that there are transitions where activities may be measured with counting errors less than ±10% before and after the occurrence of the gaseous phase radon. The transitions in Th-234 and Ra-226 can be used to monitor the relative activities of those isotopes compared to other post radon isotopes and check whether secular equilibrium exists at these two points. There have been several reports of departures from secular equilibrium in a great number of materials common to ceramics (for example, Rosholt, Shields & Garner, 1963; Irlwick, 1978; Nishimura, 1970; Scott, 1968; Meakins, <u>et al</u>, 1978; Murray & Aitken, 1980).

Table 2 compiles the information used to study secular equilibrium in material thought to exhibit this phenomenon. Here the activities of four isotopes are normalized to the activity of the 609.3-keV transition in Bi-214. Data are shown for thin samples (190 $\mathrm{mgm/cm^2}$) of radiometric standards from the Canadian Centre for Mineral and Energy Technology to see if the normalized activities are constant, as would be expected for material in secular equilibrium. The CANMET standards are thought to be in equilibrium but no guarantee is given (Ingles, <u>et al</u>, 1977). Within the range of experimental error the normalized activities for the three thin samples are the same.

The columns labeled THICK were produced from data recorded with radiometric standards, both from CANMET and IAEA, mixed with raw clay to closely simulate a ceramic. Proportions used were approximately 5 grams of standard powder to 55 grams of clay. Other than BL-1 and S-3 the normalized activities are the same indicating that we may rely on these "bench mark" normalized activities for material in secular equilibrium. BL-1 and S-3 may be slightly out of equilibrium at the points measured. Finally, the last line of Table 2 shows the ratio of the normalized activities for the Th-234 and Ra-226 transition. The ratios are consistent except for BL-1, also showing that this standard may be slightly out of equilibrium.

The use of these "bench mark" activities is shown in Table 3. The first two columns list the "bench mark" ranges. Following these are normalized activities for material we have measured for emanation loss. The first three columns are for materials that we have determined do not emanate (Carriveau & Harbottle, 1980); considering experimental error the normalized activities fall within the "bench mark" ranges. The next two columns labeled "Pitchblende" are from samples where a Pitchblende powder was mixed in two different matrices, Tennessee Ball clay and high density ceramic powder. This test was done to measure any gamma-ray absorption effects. The two cases are quite consistent, indicating that density effects are small. This Pitchblende (from Ward Scientific Co.; secular equilibrium condition unknown) shows low normalized activities for Th-234 and Ra-226.

The next three columns illustrate the use of the "bench mark" activities when measuring material for secular equilibrium and provide examples of three different cases of departure. The first, labeled Florida soil, shows data from a phosphate soil from Florida (S. Sutton, private communication). Note that the Th-234 and Ra-226 ratios are much higher than expected, suggesting reduced post-radon daughter activities. Figure 3 shows the post-emanation daughter build-up (post-radon, 50%; post-thoron, 35%) indicating significant radon and thoron losses.

The ratio of Th-234 to Ra-226 (last line in this table) is consistent with the value expected for secular equilibrium. Therefore, in this case, the larger than expected Th-234 and Ra-226 normalized activities indicate radon loss.

Next, consider the column labeled Ban Chaing; these are data from two sherds from Northeast Thailand (C. Gorman, private communication). The first two normalized ratios, Th-234 and Ra-226, are higher than would be expected from material in secular equilibrium. Figure 4 shows representative data from one sherd; this indicates neither radon nor thoron loss. The ratio Th-234:Ra-226 is also much higher than would be expected for secular equilibrium. The normalized activities in this case indicate that secular equilibrium is lost early in the decay chain. A detailed study, such as suggested by Murray (Murray & Aitken, 1980) would be necessary to accurately calculate an annual dose rate.

The final illustrative example of the use of normalized activities is the Hong Kong material discussed above. Again the Th-234 and Ra-226 normalized activities indicate departure from secular equilibrium. Figure 1 shows that there is indeed radon and thoron loss. In addition, the ratio Th-234:Ra-226 is much higher than expected, indicating non-equilibrium early in the decay chain. This combination of loss of secular equilibrium in the first few steps of the uranium decay chain plus radon and thoron loss makes this material extremely difficult, if not impossible, to work with for TL dating. Further discussion of this material may be found in the paper by Wu and Kendall (Wu & Kendall, 1980).

The final three columns (designated by an asterisk) are data taken from the large radon loss cell (Carriveau & Harbottle, 1979). These are included solely to show the effects of different geometry. The consistency of the normalized activities found in the preceding cases also holds in these examples.

The measured activities from material of known U and Th concentration may be used to determine concentration factors as shown in Table 4. Note that these values are for this specific instrument. The concentration factors are not precise enough to be used to calculate accurate annual dose rates but can be used to estimate uranium and thorium concentrations to a degree of accuracy sufficiently precise for most authenticity work.

In summary, we have presented a technique that may be used to check on secular equilibrium, with a specific measure of emanation. Through use of normalized activities obtained from the initial counting period we can obtain indications of non-equilibrium. One may then, through use of a sealed sample cell, determine precisely the amount of emanation, if present, or to indicate if non-equilibrium occurs earlier in the decay chain. The measurements can be made with the sherd in "as dug" state of water saturation to study the effect of ground water uptake on emanation.
In addition, the gamma-ray activities allow one to estimate the uranium and thorium concentrations with an accuracy sufficient for authentication tests.

All the measurements can be done in approximately the same time as alpha counting methods now in current use with the advantage that the gamma-ray results are much more accurate and complete for non-equilibrium studies.

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Table 1. Gamma-ray transitions seen in run 223104 Hong Kong sherds counted for 43.8 hours, in counts per hour. Only those transitions in the energy range 90-1800 keV were studied.

Table 2. Normalized activities from radiometric uranium ore samples. All activities are normalized to the 609.3-keV transition in Bi-214. The numbers in parentheses are one standard deviation, in percent, determined from counting statistics.
BL = CANMET series S = IAEA series

Table 3. Normalized activities from radiometric standards, sherds, clay, fly ash and soil.

Table 4. Determination of factors used to estimate uranium and thorium concentrations in sherds tested for secular equilibrium.

	Uranium Series				
	E	Activity	σ(%)	Back-ground	σ(%)
Th-234	* 92.8 92.3	66.7	8.9	9.7	17.5
Ra-226	* 186.0	37.5	7.6	7.4	23.3
Pb-214	785.95	2.9	24.0	1.1	41.5
	* 351.99	97.2	2.2	3.3	47.5
	* 295.22	61.7	3.4	–	–
Bi-214	*1120.4	12.3	8.1	3.7	19.6
	934.8	2.7	24.8	–	–
	806.3	1.9	22.6	–	–
	768.7	5.8	15.3	–	–
	666.0	3.0	29.1	–	–
	* 609.3	65.1	2.6	2.3	31.8

	Thorium Series				
	E	Activity	σ(%)	Back-ground	σ(%)
Ac-228	1588.3	4.7	33.2	–	–
	968.8	20.2	12.5	2.3	29.3
	964.4	5.9	20.6	–	–
	*911.2	27.8	4.6	2.4	26.7
	835.6	3.0	29.5	–	–
	795.0	6.1	12.8	–	–
	771.8	2.9	29.2	–	–
	463.3	10.4	12.1	–	–
	409.8	4.3	22.9	–	–
	338.7	34.0	5.2	2.6	38.7
	328.3	12.0	32.1	–	–
	270.5	16.6	11.8	–	–
	209.5	19.9	12.2	–	–
	129.1	17.0	14.9	–	–
	99.7	13.2	24.9	–	–
Ra-224	241.0	34.9	6.4	–	–
Pb-212	300.09	13.6	12.6	–	–
	*238.63	206	3.2	11.4	15.4
Bi-212	1620.56	1.0	32.3	–	–
	785.42	2.9	29.2	–	–
	727.17	11.6	10.3	–	–
Tl-208	860.5	6.0	41.4	–	–
	*583.14	51.6	3.3	6.4	45.2
	277.36	8.4	22.1	–	–

		THIN*				THICK**						
		B1-2	B1-3	BL-4	S-4	BL-1	BL-2	BL-3	BL-4	S-2	S-3	S-4
Th-234												
#1	92.8 keV	0.48	0.47	0.53	0.51	0.44	0.30	0.31	0.32	0.30	0.42	0.34
					(2.3)	(3.1)						
Ra-226												
#2	186.0 keV	0.69	0.67	0.71	0.80	0.59	0.54	0.52	0.53	0.56	0.71	0.62
					(1.7)							
Pb-214												
#3	295.22 keV	1.13	1.17	1.14	1.14	0.96	0.97	0.97	0.94	0.98	1.00	0.97
					(1.3)	(0.6)						
#4	351.99 keV	1.78	1.81	1.77	1.82	1.56	1.57	1.57	1.52	1.57	1.58	1.57
					(0.9)	(0.4)						
Bi-214												
#5	609.3 keV	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
					(1.1)	(0.5)						
#6	1120.4 keV	0.19	0.19	0.19	0.18	0.21	0.19	0.18	0.18	0.17	0.17	0.18
					(8.5)	(3.5)						
#7	1238.0 keV	0.069	0.065	0.078	0.063	0.071	0.066	0.066	0.065	0.064	0.062	0.064
					(5.9)	(2.6)						
					#1:#2	0.74	0.56	0.60	0.60	0.54	0.59	0.55

* All samples = 190 mgm/cm^2 on 1 mm Al backing

** All samples contained in 70 c.c. (7 cm dia, 18 mm) glass cell

Isotope	Energy (keV)	CANMET Series	IAEA Series	Túyere Sherds	Tennessee Ball Clay	Fly Ash	Pitchblende + TBC	Pitchblende + Túyere	Florida Soil	Ban Chaing 988 & 2114	Hong Kong Sherds	Amphorae* Sherds	Texoloc* Sherds	Túyere* Sherds
Th-234	92.8	0.30-0.44	0.30-0.42	0.43	0.35	0.35	0.22	0.22	0.84	0.86-0.94	1.32	0.29	0.26	0.23
Ra-226	186.0	0.52-0.59	0.56-0.71	0.52	0.47	0.50-0.57	0.42	0.43	1.20	0.73-0.83	1.02	0.44	0.53	0.43
Pb-214	295.22	0.94-0.97	0.97-1.00	0.83	0.76	0.85-0.93	0.87	0.86	0.95	0.89-0.98	0.91	0.79	0.81	0.82
	351.99	1.52-1.57	1.57-1.58	1.40	1.30	1.44-1.52	1.45	1.43	1.56	1.53-1.64	1.52	1.34	1.34	1.38
Bi-214	609.3	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	1120.4	0.18-0.21	0.17-0.18	0.20	0.23	0.19-0.20	0.19	0.20	0.18	0.20-0.22	0.21	0.20	0.21	0.20
	$\frac{\text{Th-234}}{\text{Ra-226}}$	0.64	0.58	0.83	0.74	0.65	0.52	0.51	0.70	1.15	1.29	0.66	0.49	0.53

* Data taken with large volume cell (Carriveau & Harbottle, Archaeo Physiko 10, 423-427, 1979). All other data taken with 70 c.c. glass cell and lead shield.

Table 4.

Uranium*		Thorium**	
BL-1	74	Tennessee Ball Clay	45
BL-2	73	Tuyere	51
BL-4	66	Tennessee Fly Ash	36
S-3	61	Ban Chaing Group	47
S-4	71		

<u>Average</u>:

$$69 \pm 5 \ \frac{\text{counts}}{\text{hour-kgm-ppm UO}_3} \qquad 45 \pm 6 \ \frac{\text{counts}}{\text{hour-kgm-ppm ThO}_2}$$

* Activity data taken from the Ra-226 transition at 186.0 keV.

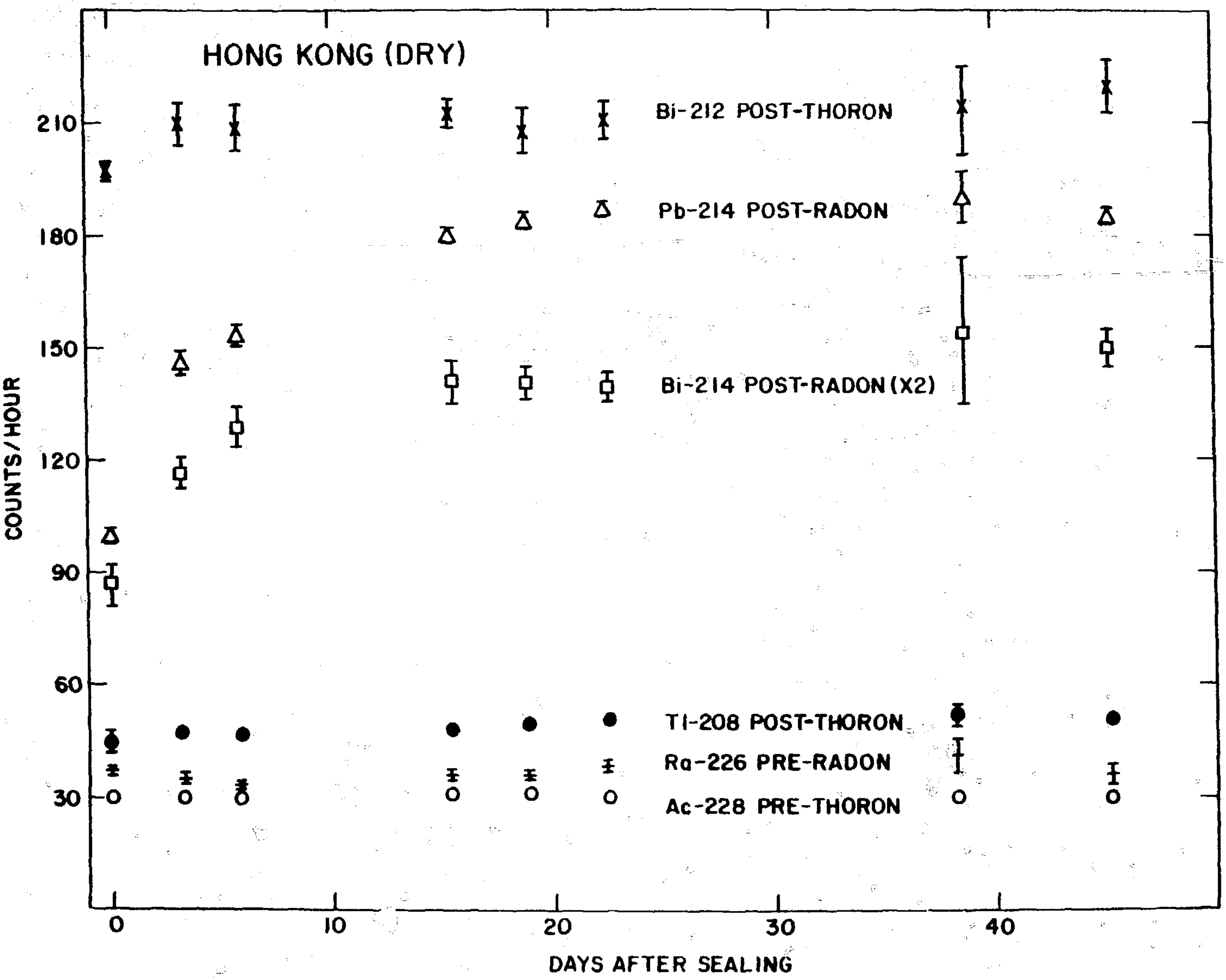
**Activity data taken from the Ac-228 transition at 911.2 keV.

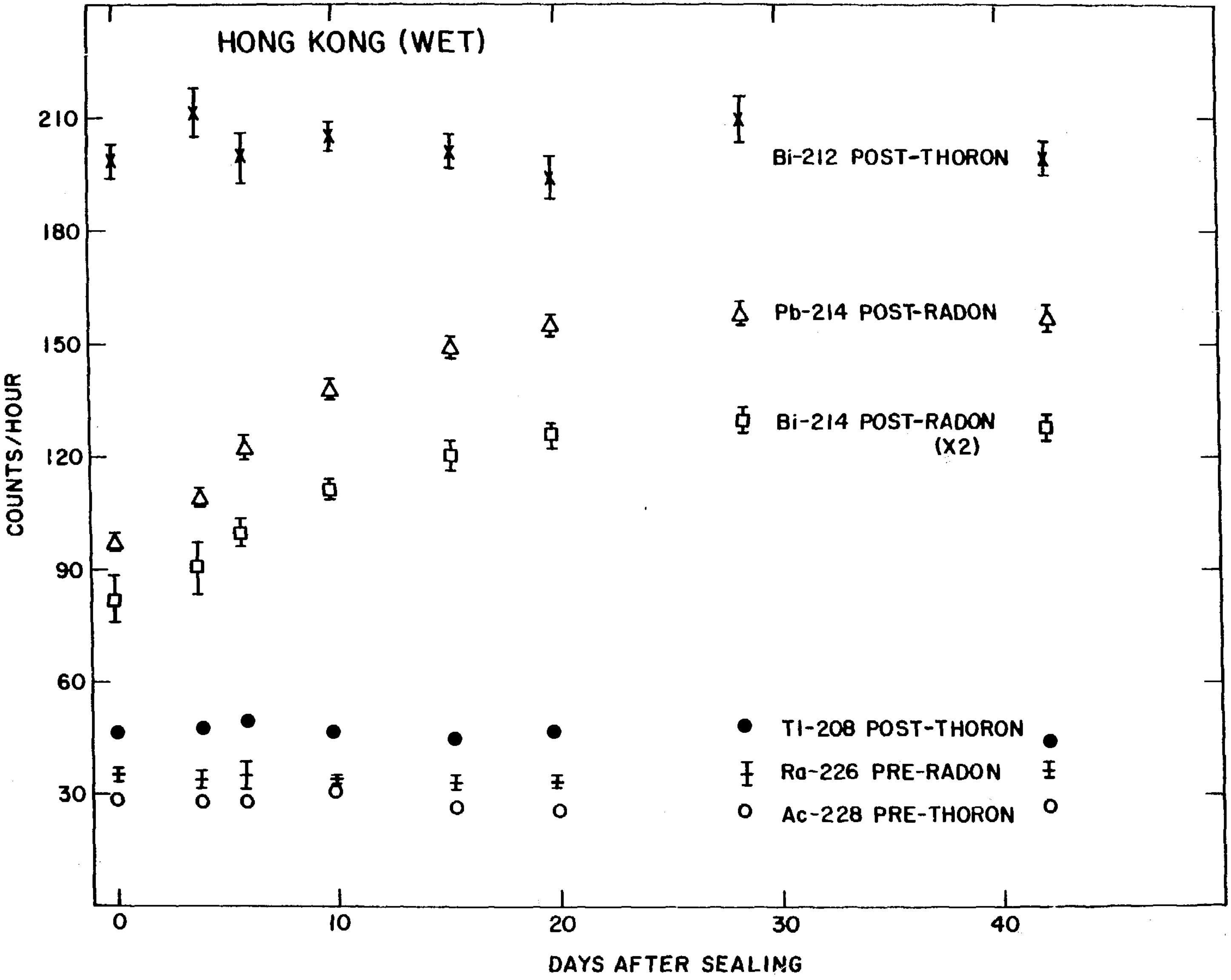
Figure 1. Count rate vs time after sealing for represenative material from Hong Kong. The sherds were dried in an oven at 70°C for 24 hours. Error bars represent ±σ determined from counting statistics.

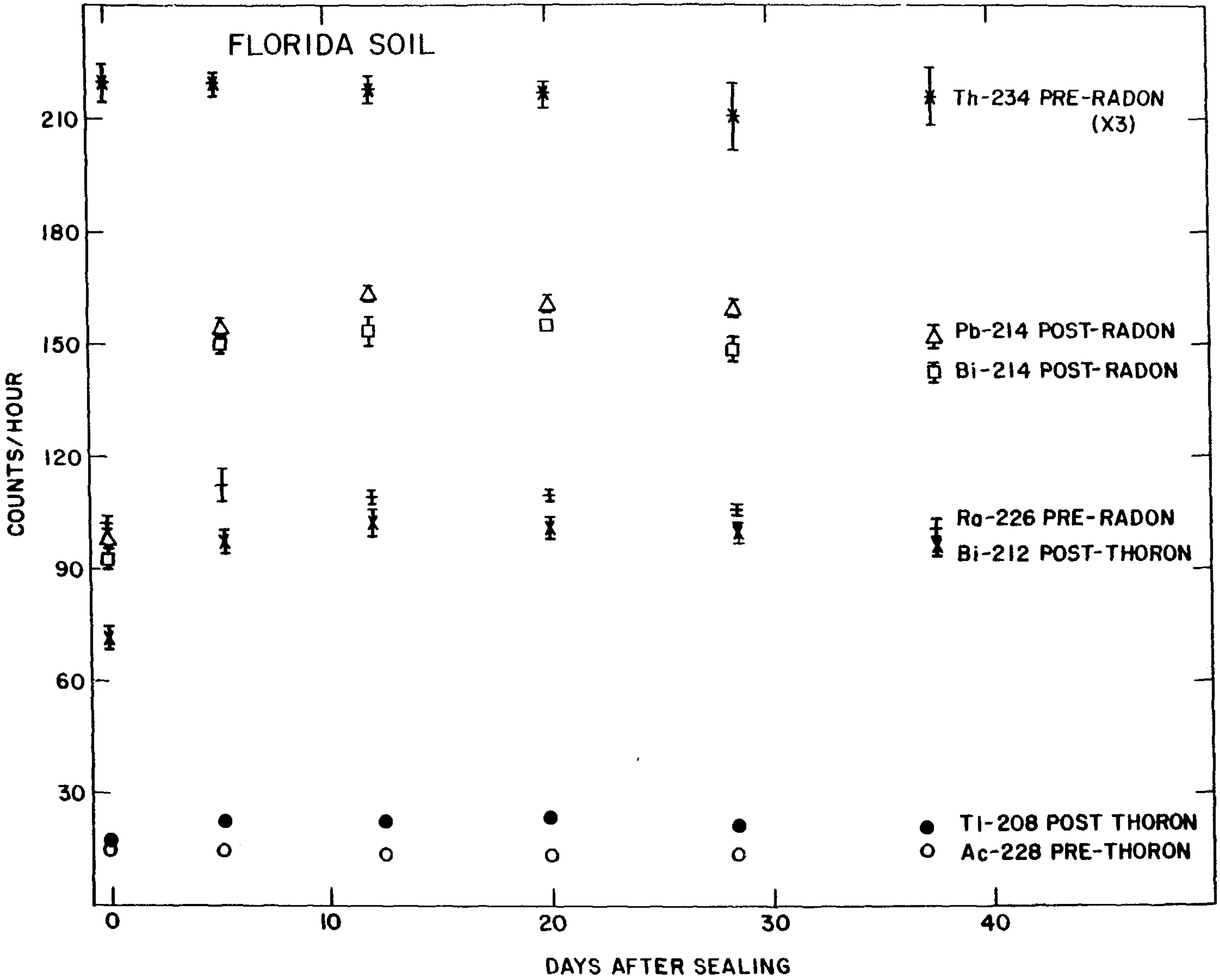
Figure 2. Count rate vs time after sealing for representative material from Hong Kong. Saturated water uptake equals 11.7% dry weight.

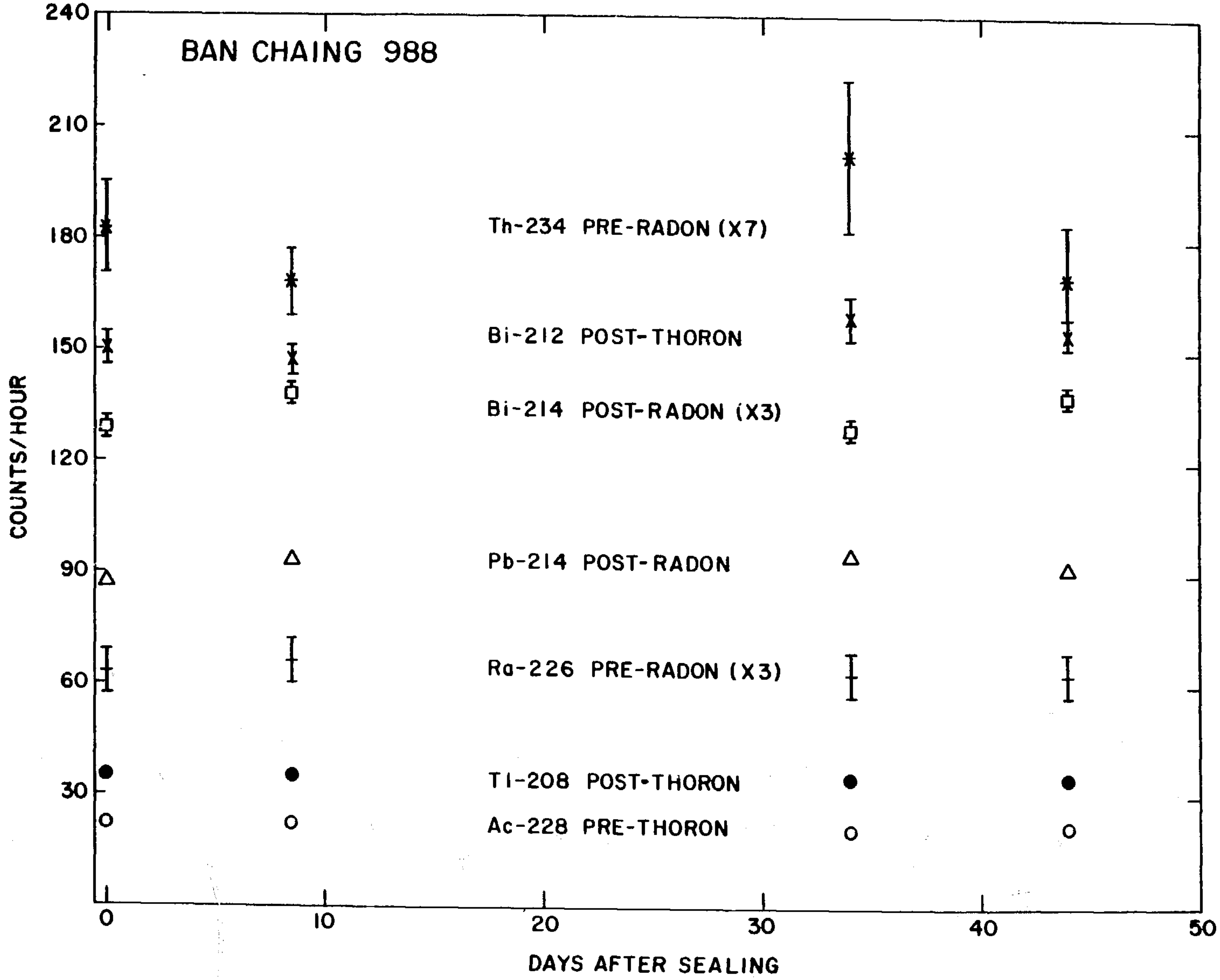
Figure 3. Count rate vs time after sealing for dry Florida soil. Error bars represent ±σ determined from counting statistics.

Figure 4. Count rate vs time after sealing for dry Ban Chaing sherd 988. Error bars represent ±σ determined from counting statistics.


HONG KONG (DRY)
Bi-212 POST-THORON
Pb-214 POST-RADON
Bi-214 POST-RADON (X2)
Tl-208 POST-THORON
Ra-226 PRE-RADON
Ac-228 PRE-THORON
COUNTS/HOUR
210
180
150
120
90
60
30
0
10
20
30
40
DAYS AFTER SEALING

HONG KONG (WET)
COUNTS/HOUR
210
180
150
120
90
60
30
0
10
20
30
40
DAYS AFTER SEALING
Bi-212 POST-THORON
Pb-214 POST-RADON
Bi-214 POST-RADON (X2)
Tl-208 POST-THORON
Ra-226 PRE-RADON
Ac-228 PRE-THORON


FLORIDA SOIL
COUNTS/HOUR
210
180
150
120
90
60
30
0
10
20
30
40
DAYS AFTER SEALING
Th-234 PRE-RADON (X3)
Pb-214 POST-RADON
Bi-214 POST-RADON
Ra-226 PRE-RADON
Bi-212 POST-THORON
Tl-208 POST THORON
Ac-228 PRE-THORON


BAN CHAING 988
Th-234 PRE-RADON (X7)
Bi-212 POST-THORON
Bi-214 POST-RADON (X3)
Pb-214 POST-RADON
Ra-226 PRE-RADON (X3)
Tl-208 POST-THORON
Ac-228 PRE-THORON
COUNTS/HOUR
240
210
180
150
120
90
60
30
0
10
20
30
40
50
DAYS AFTER SEALING