Palaeont. afr., **23**, 41–44 (1980)

DATING POSSIBILITIES FOR THE SOUTH AFRICAN HOMINID SITES

by

J.C. Vogel

National Physical Research Laboratory, C.S.I.R., Pretoria.

ABSTRACT

A brief description is given of dating methods which may in future prove to be applicable to the calcified ossiferous cave deposits of the early hominid sites in the Transvaal. Potentially the techniques based on amino acid racemisation, uranium series disequilibrium and radiation damage could provide dates for at least the upper members of the cave formations. The results would, however, have to be calibrated in the younger time-range by radiocarbon dating of parallel samples.

INTRODUCTION

There is at present no well established dating method that can be applied to the hominid sites in southern Africa, but there are techniques under investigation which hold out hope for the future. The prospects of some of the new methods which can be applied to calcified ossiferous cave deposits will be discussed briefly.

AMINO ACID RACEMISATION

The collagen contained in bone can be used for dating by means of the racemisation reaction of individual amino acids that constitute the protein molecule. The optically active amino acids produced by living organisms are mainly laevorotatory (L-) and these L-forms gradually change into the dextrorotatory (D-) forms until an equilibrium ratio is reached. The racemisation reactions are extremely slow at ambient temperatures so that the extent of racemisation, that is the D/L ratio of a specific amino acid isolated from collagen, can be used to estimate the age of a bone.

The rate of racemisation is highly temperature dependent: an increase of about 3,5 °C will double the rate so that the correct assessment of the average temperature to which the sample has been subjected since deposition is rather critical. In practice it has been found that it is more reliable to determine the empirical rate constant for a site by analysing radiocarbon dated samples (preferably of about 20 000 yrs old) and use this to estimate the age of the deeper levels (Bada *et al.*, 1974).

The two amino acids that have been thoroughly investigated for dating purposes are aspartic acid and isoleucine. The latter has the slowest known rate of racemisation — or in this case, more correctly, of epimerisation. The rate constants as determined on bone samples (Bada 1972, Bada *et al.*, 1973) give the half-lives of the L-amino acid and the effective range of dating as listed in Table 1. The calculated age/ratio development is shown in Figures 1 and 2.

TABLE 1
Estimated Half-Life and Range for Racemisation-Epimerisation Reactions.

	$t_{½}$ (yrs)*		t_{max} (yrs)†	
	15 °C	20 °C	15 °C	20 °C
Aspartic acid	28 000	11 000	140 000	51 000
Isoleucine	280 000	100 000	1 830 000	670 000

* Half-life of L-aspartic acid is time required to reach a D/L ratio of 0,33; for L-isoleucine it is the time required to reach an alloisoleucine/isoleucine ratio of 0,345 because the end-value is 1,38, not 1.

† Maximum age taken as time to reach 95 % of equilibrium value.

It would thus appear that the range of this method is too short for the effective dating of our hominid sites. There is, however, evidence that the amino acids bound in collagen racemise more slowly than do free amino acids (Bada 1972) and that a much higher age-range will be attained if only the intact collagen is used for analysis. This would also be much more reliable than analysing

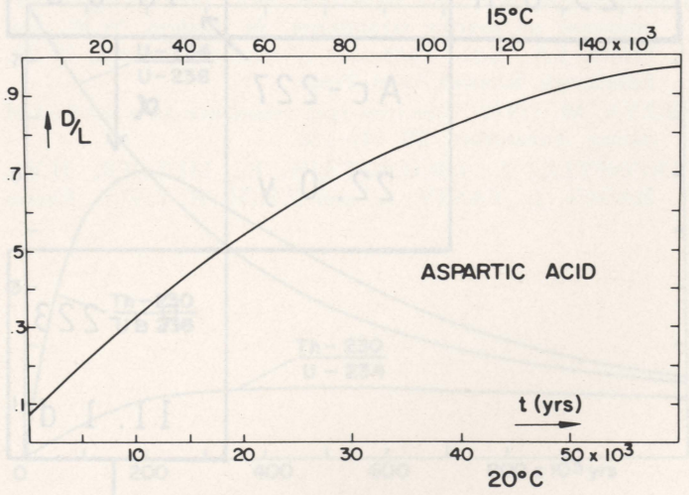


Figure 1. Calculated change of D/L ratio of aspartic acid with time for 15 °C (top scale) and 20 °C (bottom scale).

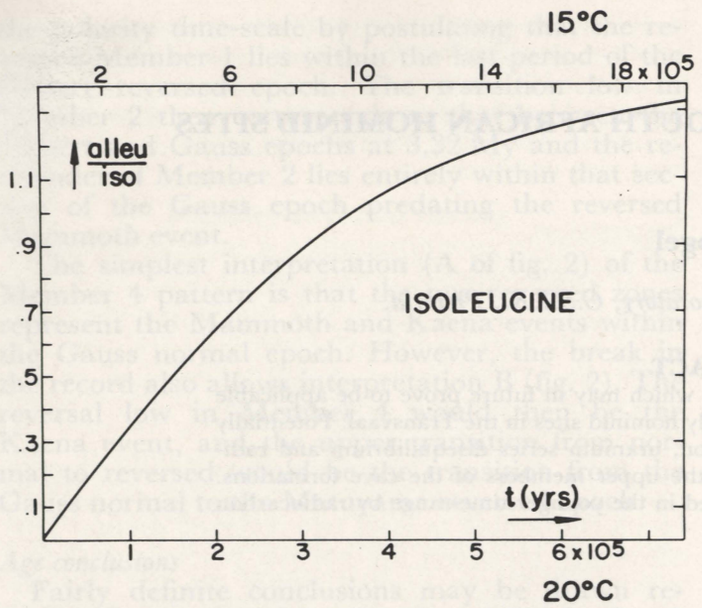
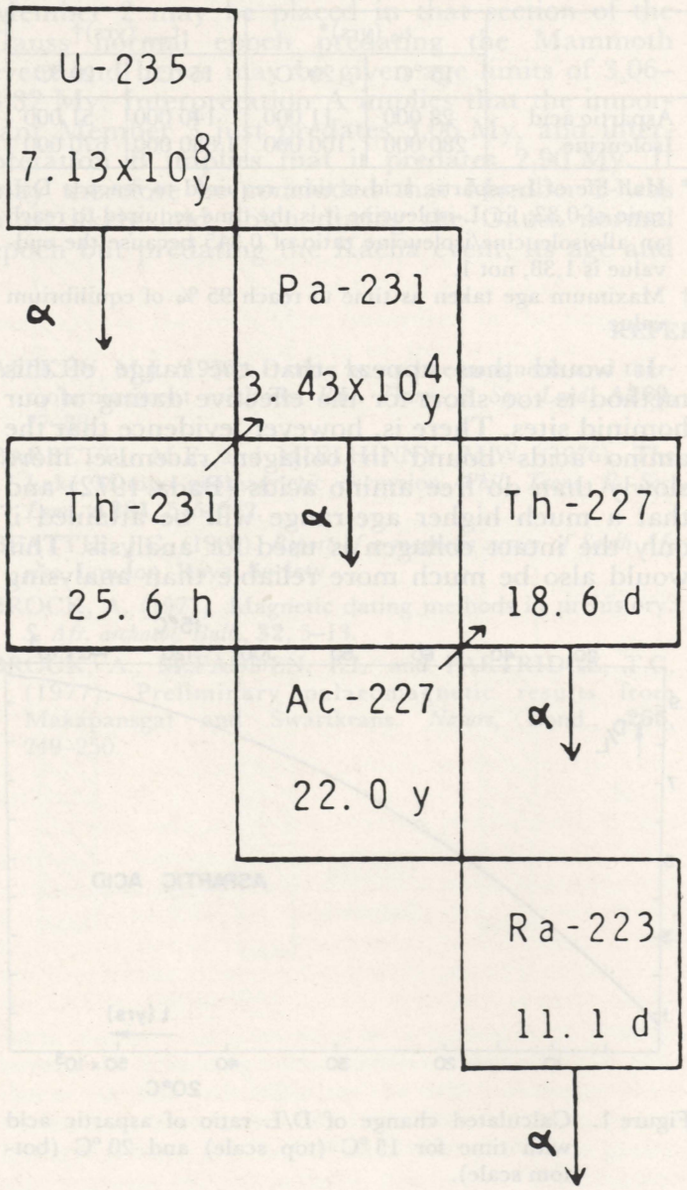


Figure 2. Calculated change of D-alloisoleucine/L-isoleucine ratio with time for 15 °C (top scale) and 20 °C (bottom scale).



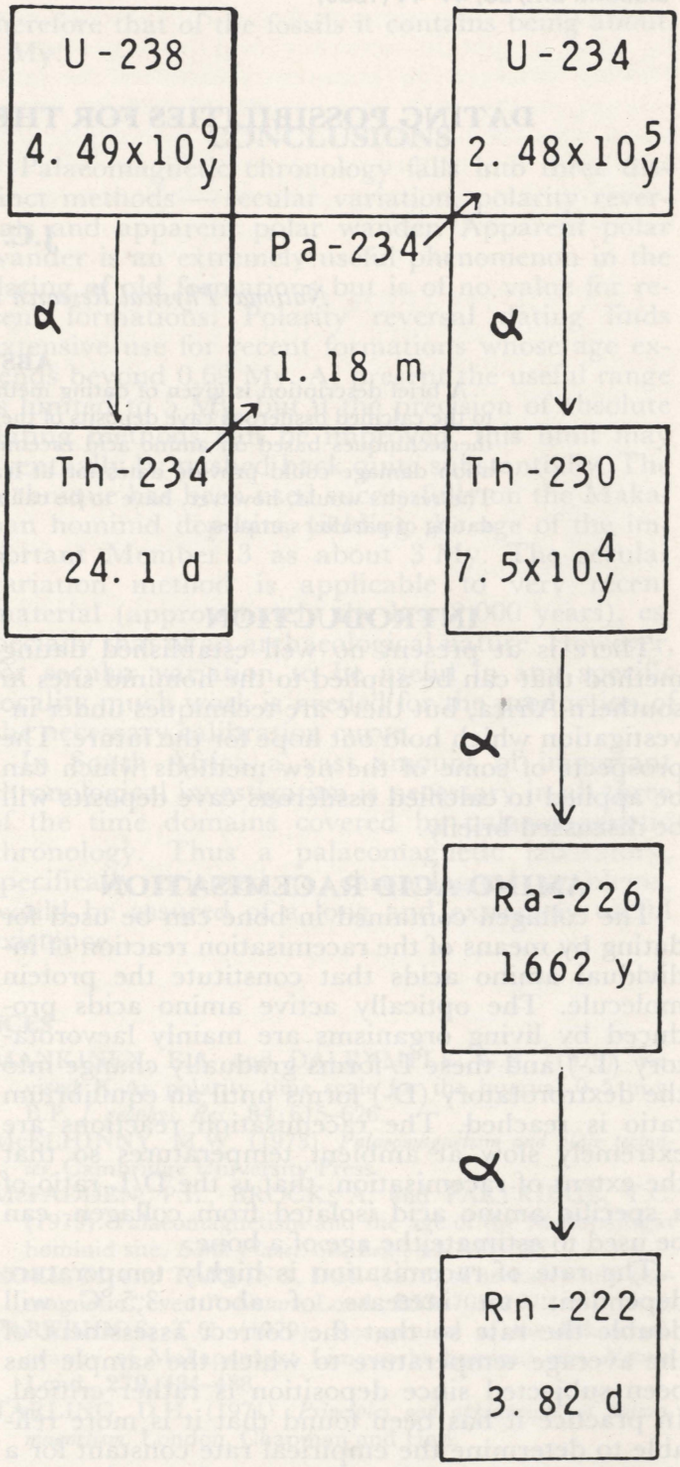


Figure 3. Initial portions of the U-238 and U-235 decay schemes showing the long-lived isotopes U-234, Th-230 and Pa-231 used for dating Pleistocene events.

the total organic component of a bone, since it is known that secondary amino acids are frequently present in fossil bone. That such contamination is a serious problem is evident when a date for a bone from Swartkrans is calculated from Bada's measurement of the alloisoleucine/isoleucine ratio of 0,37 (Bada *et al.*, 1973). Assuming the average temperature to be 15 °C, the age obtained is

300 000 years. It remains, of course, to be established whether any collagen can still be isolated from these very ancient bones.

URANIUM SERIES DISEQUILIBRIA

The dating of Pleistocene calcium carbonate deposits is made possible by disturbances in the radiation equilibrium that exists between uranium and its radioactive daughter isotopes. Three of these have sufficiently long half-lives to be potentially useful (Broecker and Bender 1972, Ku 1976), namely:

Protactinium-231, $t_{1/2}$ = 34 300 yrs (U-235-series)
Thorium-230, $t_{1/2}$ = 75 200 yrs (U-238-series)
Uranium-234, $t_{1/2}$ = 248 000 yrs (U-238-series)

The relevant portions of the decay schemes are shown in Figure 3.

Ionium (Th-230) deficiency

The basis of this method of dating carbonates is that thorium is extremely insoluble in water and is rapidly removed by adsorption on solid surfaces. The result is that groundwater contains small amounts of dissolved uranium but virtually no thorium. Calcium carbonate deposited from such waters thus incorporates some uranium but little or no Th-230. The concentration of this latter isotope then gradually increases at a rate corresponding to its half-life until eventually the production rate equals the rate of decay, that is the activity ratio T-230/U-234 is unity (fig. 4).

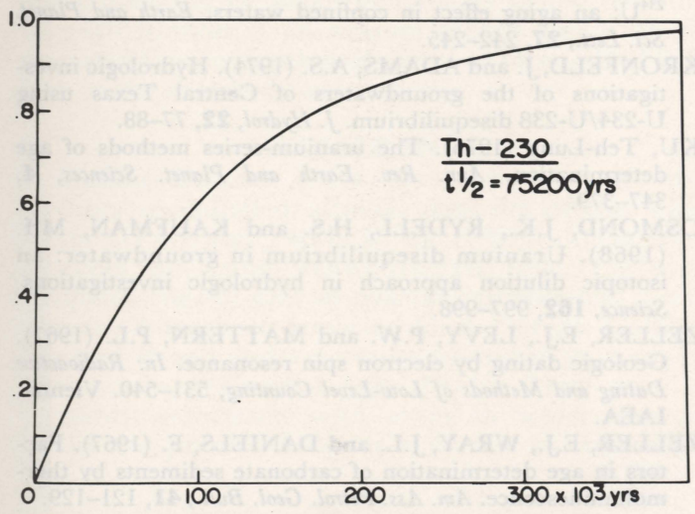


Figure 4. Growth of the activity ratio Th-230/U-234 in the case that the U-234 is in radiation equilibrium with U-238.

Provided the mineral has remained a closed system with no addition or loss of parent or daughter and the initial concentration of the daughter isotope was zero, the age can be obtained from measurement of the isotope ratio. The well-known technique for dating deep-sea sediments with these isotopes is different in that there the *decrease* in Th-230 is measured, not the *build-up*.

A complication arises in this dating method in that the U-234 is not necessarily in radiation equilibrium with the long-lived parent, U-238, so that the U-238/U-234 ratio must also be measured, and the calculation of the age becomes somewhat more complicated. The content of the long-lived Th-232 must also be assayed since this indicates to what extent Th-230 would initially have been present in the sample: if the Th-232 content is low, the dating is more reliable.

The principle of protactinium, Pa-231, dating is the same as that for ionium dating outlined above, but the concentration of U-235 is lower and the half-life of Pa-231 is shorter.

The dating range of the ionium method is restricted to 300 000–400 000 yrs and it is thus not of much interest for the hominid sites. There is, however, a possibility of extending the range to some extent by making use of the U-234/U-238 disequilibrium.

Uranium-234 excess

It sometimes happens that the U-234/U-238 activity ratio in groundwater is considerably greater than unity. Values of 10 or even 20 have been observed (Osmond *et al.*, 1968, Kronfeld and Adams 1974, Kronfeld *et al.*, 1975). This isotopic effect is caused by the differential leaching of U-234 as a result of the dislocation of the atom in the crystal by a recoil of the parent isotope during decay. Direct injection of the atoms into the water also occurs and is probably mainly responsible for the higher isotope ratios that have been encountered. The uranium isotopic mixture incorporated in the crystals during calcium carbonate precipitation will then gradually return to an activity ratio of unity with a half-life of 248 000 yrs (fig. 5).

The U-234/U-238 ratio can thus potentially produce dates up to or beyond 1 My. The problem is that the initial ratio is not known *a priori*, but, if younger sections of a calcite deposit can be dated by Th-230 and this indicates an initial uranium

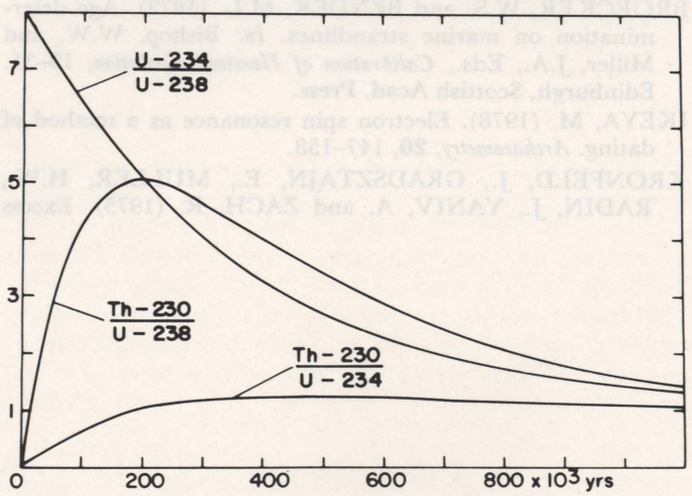


Figure 5. Change in activity ratios of isotopes with time for a sample with, initially, U-234/U-238 = 8 and zero Th-230.

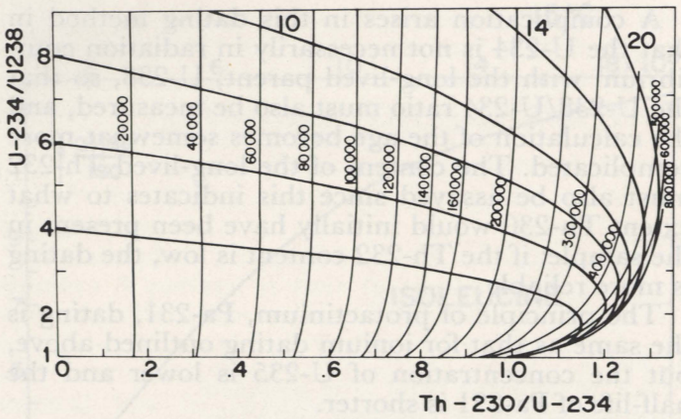


Figure 6. Uranium-series disequilibrium plotted as a function of time.

isotope ratio that remained constant with time, extrapolation to older samples would be possible (fig. 6).

Relatively high U-234/U-238 ratios of five to eight have been found in speleothems from Wolkberg Cave east of Pietersburg (Kronfeld pers. comm.), and this arouses the expectation that other cave sites in the Transvaal may exhibit similar high ratios. We are at present investigating whether such favourable conditions do in fact exist at the hominid sites, and some dates may be forthcoming — albeit only of the younger sections of the sequences.

RADIATION DAMAGE

Damage caused in the crystal structure of a mineral by radiation associated with radioactive decay is utilized in different ways to provide age estimates. The simplest technique in this category of dating methods is that of counting the number of *fission tracks* in a polished and etched section of a mineral and comparing the count with the number of tracks induced artifically in a nuclear reactor. The method does not, however, appear to be applicable to calcite.

The other two methods determine the total radiation dose experienced by the sample either by *thermoluminescence* or by *electron spin resonance* techniques and compare this with the annual dose caused by the natural radioactive elements present. The measurement of the total dose is relatively straightforward, but it is very difficult to derive an accurate figure for the annual rate of the natural radiation dose. Consequently the most promising procedure seems to be the relative dating of a sequence and subsequent calibration by radiocarbon dating of the younger sections.

Both these methods are applicable to speleothems and possibly also to limestone breccias (Zeller *et al.*, 1957, Zeller *et al.*, 1967, Ikeya 1978), and there seems to be no problem of saturation for several million years. These techniques for dating Pleistocene deposits are, however, still in the experimental stage and need to be refined before they can be applied with confidence.

REFERENCES

BADA, J.L., SCHROEDER, R.A., PROTSCH, R. and BERGER, R. (1974). Concordance of collagen-based radiocarbon and aspartic-acid racemization ages. *Proc. Nat. Acad. Sci. U.S.A.*, **71**, 914–917.

BADA, J.L. (1972). The dating of fossil bones using the racemization of isoleucine. *Earth and Planet. Sci. Lett.*, **15**, 223–231.

BADA, J.L., KVENVOLDEN, K.A. and PETERSON, E. (1973). Racemization of amino acids in bones. *Nature* Lond., **245**, 308–310.

BROECKER, W.S. and BENDER, M.L. (1972). Age determination on marine strandlines. *In:* Bishop, W.W. and Miller, J.A., Eds., *Calibration of Hominid Evolution,* 19–35. Edinburgh, Scottish Acad. Press.

IKEYA, M. (1978). Electron spin resonance as a method of dating. *Archaeometry,* **20**, 147–158.

KRONFELD, J., GRADSZTAJN, E., MULLER, H.W., RADIN, J., YANIV, A. and ZACH, R. (1975). Excess ^{234}U: an aging effect in confined waters. *Earth and Planet. Sci. Lett.*, **27**, 242–245.

KRONFELD, J. and ADAMS, A.S. (1974). Hydrologic investigations of the groundwaters of Central Texas using U-234/U-238 disequilibrium. *J. Hydrol,* **22**, 77–88.

KU, Teh-Lung (1976). The uranium-series methods of age determination. *Ann. Rev. Earth and Planet. Sciences,* **4**, 347–379.

OSMOND, J.K., RYDELL, H.S. and KAUFMAN, M.I. (1968). Uranium disequilibrium in groundwater: an isotopic dilution approach in hydrologic investigations. *Science,* **162**, 997–998.

ZELLER, E.J., LEVY, P.W. and MATTERN, P.L. (1967). Geologic dating by electron spin resonance. *In: Radioactive Dating and Methods of Low-Level Counting,* 531–540. Vienna, IAEA.

ZELLER, E.J., WRAY, J.L. and DANIELS, F. (1967). Factors in age determination of carbonate sediments by thermoluminescence. *Am. Ass. Petrol. Geol. Bull.,* **41**, 121–129.