

Suggestions for minimum requirements for reporting ESR age estimates

Rainer Grün

Radiocarbon Dating Research Unit, RSPacS, ANU, GPO Box 4, Canberra ACT 2601, Australia.

Although ESR spectrometry has been applied as a dating technique since 1975 (Ikeya 1975), there are no standards for the citation of ESR age estimates, not even any minimum requirements. It is therefore not surprising that the quality of the published procedures and analytical results for ESR age estimates vary to a great extent. In many cases ESR dating papers give little information about the estimation of the dose, D_E , or the dose rate, \dot{D} , that the sample received in its geological past. In order to establish ESR as a mature dating technique, it is necessary to standardize the citation procedures to some extent. It must be the aim of such a standardization, that new ESR age estimates are published with all analytical values and their errors so that the results can be reproduced/recalculated by any ESR specialist. Sufficient detail can either be given in the publication containing new age estimates or in a separate ESR data list as has been done for ^{14}C and TL age estimates in the journals *Radiocarbon* and *Ancient TL*, respectively.

Additionally, there is no agreement on the terminology used in ESR dating. The use of the acronym AD for either accumulated dose and annual dose should certainly be avoided. Additionally, it is not common practice in physics or mathematics to abbreviate a single parameter by two or more characters in sequence. It seems advantageous to adopt the terminology analogous to that of TL dating. This paper tries to outline the minimum requirements for the citation of ESR age estimates and to suggest appropriate terminology for use in ESR dating papers. It should be noted here, that the scientific committee of the TL and ESR Dating Seminars have agreed that minimum citation requirements and terminologies have to be established prior to the next meeting in Vienna 1993 and that contributions for the conference proceedings ought to follow these guidelines. Rather than being a critique of the terminology that has been forwarded by Aitken (1992) this paper intends to broaden the base for discussion.

An ESR age estimate involves basically three procedures: the determination of the radiation dose that a sample has received in the past using ESR spectrometry, the estimation of the dose rate by various different techniques and the assessment of the error. The

significance of the last procedure is not often fully appreciated.

Determination of the past radiation dose, D_E

The parameter that is actually determined by ESR spectroscopy is the past radiation dose. This is the energy dose that was transferred to the mineral by ionizing radiation and the SI unit is the gray (Gy) (see e.g. The Symbols Committee of the Royal Society, 1975). This parameter is usually determined by the additive dose technique using gamma radiation from a ^{60}Co or ^{137}Cs source. The result is therefore the absorbed gamma equivalent dose which may be expressed by either D_E or $D_{E\gamma}$. The term equivalent dose, ED, is not strictly correct, since this is reserved in radiation protection for the radiation dose equivalent to humans and would have the unit sievert (Sv) (see e.g. Handbook for Chemistry and Physics).

It does not seem to be a great problem to determine a D_E value with the additional dose method (i.e. the intersect of the X-axis at $I=0$) either with linear or exponential fitting procedures. However, since the number of traps is limited, the trapping probability changes as traps are progressively occupied by electrons or holes and hence it is unlikely that linear fitting is the correct description of a dose response. In some cases, e.g. corals (Grün 1990), the dose response can only be described by a more complicated mathematical expression. Consequently, the mathematical model behind the curve fitting must be reported (and justified by observation).

There is no general recipe of how many different aliquots have to be measured and to which doses these aliquots should be exposed in order to obtain reliable D_E values (one might get some idea about this from the computer simulations of dose response curves (Grün & Rhodes 1991)). It is therefore necessary to cite how many aliquots and which dose steps were used for the estimation of D_E . If the ESR intensity values, I , scatter around the best fit, the D_E value is dependent on the weights, w , assigned to the intensity values. Grün & Macdonald (1989) used equal weights ($w=1$) whereas Berger & Huntley (1986) and Berger et al. (1987), suggested in TL studies the use of weights proportional to the inverse square of the measured intensity (i.e. $w \sim I^{-2}$, which arises from the assumption that each

ESR/TL intensity measurement has the same relative uncertainty).

Many materials such as carbonates (see Debuyst et al. 1990, 1991, Barabas 1989, Barabas et al. 1992a,b) have several ESR signals that are radiation sensitive. Hence, it has to be reported which paramagnetic centre was used for the D_E determination and how it was measured. Since D_E results derived from a particular paramagnetic centre may be dependent on the measurement conditions, such as microwave power or the resolution of the ESR spectra (see e.g. Molodkov 1988, Barabas 1989), it is necessary to cite the following parameters:

- the approximate microwave frequency, ν , in GHz or frequency band of the ESR spectrometer;
- the microwave power in mW (a dB value is related to the maximum microwave power of an ESR spectrometer and this may change from instrument to instrument). Additionally, the effective microwave power at the sample position is dependent on the sample holder, e.g. when using a double walled quartz tube, the microwave power at the sample may be twice the adjusted power;
- the scan width in tesla (T) and scan time or by combining both the scan speed;
- the modulation frequency in Hz;
- the modulation amplitude in T (often given in mTpp);
- the time constant in s.

Since it may be assumed that the spectrometer was optimally tuned before measurement, it seems unnecessary to quote the detection phase. If new materials or centres are discussed, a high resolution ESR spectrum should be shown and the g -values and line widths have to be given. It is not particularly useful to cite (instead of g -values) the microwave frequency, the magnetic field strength at the centre of the scan and the scan width so that the reader can calculate ones own g -values. If one prefers to use terms such as A, B, C... or $h_1, h_2, h_3...$ etc., centres, these have to be defined with g -values in a figure.

Errors in D_E estimation

There does not seem to be any agreement as to which method provides correct 1σ errors in the D_E estimation. Computer simulations of dose response curves (Grün & Rhodes 1991) imply that an error estimated on the straight line conversion of an exponential function gives errors that are significantly smaller than 1σ , whereas the jackknifing procedure (as suggested by Grün & Macdonald 1989) results in errors larger than 1σ . Additionally, the magnitude of the error seems to be dependent on the number of measurements and where these are placed in the dose response curve. More sophisticated error procedures as suggested by Berger et al. (1987) and Brumby (1992) seem to lead to consistent

error estimates. It would be worthwhile to check them in computer simulations. Additionally, the radioactive source used for the artificial irradiation has a calibration error in the range of 3 to 5% as shown in the Second Interlaboratory Comparison Project on ESR dating (Barabas et al. 1992c). Although it may be assumed that dose values obtained by alanine or Fricke dosimetry are correctly converted into calcite, sulphate, quartz or apatite doses. This should be mentioned in the paper.

Determination of the dose rate, \dot{D}

The dose rate is defined in the Handbook of Physics and Chemistry as \dot{D} . If an agreement can be reached between the ESR and TL communities, that D_E or another character can be reserved for the absorbed dose, D could be used for the dose rate. This would have the advantage that one does not have to produce the dot on the D , an inconvenient procedure for standard computers. An alternative could be the German notation D' (D prime). In order to distinguish dose and dose rate parameters more clearly, in the following text \dot{D} stands for dose rate. Alpha, beta and gamma dose rates may be denoted by subscripts ($\dot{D}_{\alpha,\beta,\gamma}$).

Both notations, \dot{D} and D' , suggest an instantaneous dose rate. However, most Quaternary samples show radioactive disequilibria and the cited dose rates are usually average dose rates over the calculated age of the sample. In these cases a notation implying a derivative is not strictly correct.

The dose rate is determined by the analysis of the radioactivity in the sample and its surrounding. This can either be done by measuring the total alpha or beta activities or by the analysis of the radioactive elements. The latter values have to be converted into dose rates by using published tables. It must be noted that these tables (e.g. Bell 1976, 1977, 1979, Hennig & Grün 1983, Nambi & Aitken 1986 or Berger 1988) have different conversion factors and the respective publication has to be cited.

It should be noted which analytical techniques were used and which parameters were assumed or taken from literature (e.g. water content, $^{234}\text{U}/^{238}\text{U}$ ratio or α -efficiency). Depending on the symmetry, a different set of parameters has to be measured.

In general the following parameters have to be reported:

Cosmic dose rate, \dot{D}_{cos} : the cosmic dose rate can either be measured with calibrated gamma spectrometers or derived from the thickness of the overlying sediment (Prescott & Hutton 1988).

Alpha efficiency: this value is very rarely measured in ESR dating studies and the discussion whether to use a k -value (Zimmerman 1972), an a -value system (see Aitken 1985) or a b -value system (Bowman & Huntley 1984, Huntley et al. 1988) etc. is rather academic.

However, it has to be reported which value has been used or why a particular α -efficiency was assumed (e.g. taken from literature). The following measured α -efficiencies have been reported: $g=2.0007$ in corals: 0.06 ± 0.01 (Radtko & Grün 1988) and 0.05 ± 0.01 (Grün et al. 1992); $g=2.0007$ in foraminifera: 0.079 ± 0.008 ; $g=2.0036$ in foraminifera: 0.093 ± 0.009 (Mudelsee 1990, Mudelsee et al. 1992); $g=2.0007$ in speleothems: 0.052 ± 0.026 (Lyons & Brennan 1991); $g=2.0018$ in tooth enamel: 0.15 (Grün 1985; DeCanniere et al. 1986).

Radioactive disequilibria: Most samples that are investigated in dating studies, such as secondary carbonates or tooth enamel, show disequilibria in the U-decay chains. This can be mathematically considered (for the respective formulae see e.g. Grün, 1989). Additionally, many samples show $^{234}\text{U}/^{238}\text{U}$ ratios of greater than unity. This is rarely measured. In some cases it may be derived from U-series measurements (e.g. secondary carbonates in sea water have the initial $^{234}\text{U}/^{238}\text{U}$ ratio of 1.14 ± 0.01 : Chen et al. (1986)). An assumed value of 1.2 ± 0.2 should normally not lead to large systematic errors. However, one has to be aware that in some areas strong $^{234}\text{U}/^{238}\text{U}$ disequilibria may occur (see e.g. multiple dating study in Egypt by Wendorf et al. 1990: $^{234}\text{U}/^{238}\text{U} \ll 1$!).

External gamma dose rate, \dot{D}_γ The external gamma dose rate cannot be assumed. It can be measured by a portable gamma spectrometer or TL dosimeters. Both techniques have a calibration error which is usually in the range of 5 to 7%. Sometimes \dot{D}_γ is derived from the analysis of the radioactive elements in the sediment. However, this approach can only be used for very homogeneous sediments (such as loess) and may lead in other cases to significant errors. The analytical technique has to be mentioned along with any further information about radioactive disequilibria.

The dose rate of a sample is strongly dependent on its size, because of the different ranges of alpha, beta and gamma rays. One can distinguish four principal cases:

1) Infinitely thick (homogeneous) samples (>60 cm, e.g. corals): the total dose rate (except cosmic) is generated by the sample. From the analysis of the radioactive elements (namely U, Th, K), the α , β , and γ dose rates are derived. Corals, for example, contain only small amounts of Th and K. It should be reported if these have been neglected. It is always worthwhile to check whether the calculated gamma dose rate can be confirmed by measurements. The following parameters have to be determined:

- U, Th, K and water contents of the sample.
- U-series disequilibria (i.e. $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$)
- α -efficiency
- cosmic dose rate

2) Thick samples (≥ 6 mm and < 60 cm, e.g. mollusc shells): the outer 2 mm can be removed and the sample receives only external \dot{D}_γ . If the sample is thicker than a few cm, the measured external gamma dose rate is attenuated by the sample and this effect has to be considered. For preliminary results on grains see Mejdahl (1983), for layers see Aitken et al. (1985). The following parameters have to be determined:

- U, Th, K, and water contents of the sample
- U-series disequilibria (i.e. $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$)
- α -efficiency
- gamma self-irradiation
- external gamma dose rate
- gamma attenuation
- cosmic dose rate

3) Medium samples (>200 μm and <6 mm, e.g. tooth enamel): it is possible to remove about 20 μm to eliminate the external alpha dose rate, however, the sample receives a portion of the external beta dose rate. Beta particles are attenuated and this attenuation has to be considered in the dose rate calculation. For beta attenuation in grains see Mejdahl (1979), for thin layers see Grün (1986). The beta emitters in the immediate surroundings of the sample (generally within 2mm) have to be determined along with the following values:

- U, Th, K and water contents of the sample
- U-series disequilibria (i.e. $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$)
- α -efficiency
- beta self-irradiation
- external beta dose rate (U, Th, K and water of the immediate surroundings)
- beta attenuation
- external gamma dose rate
- cosmic dose rate

4) Small samples (< 200 μm , e.g. foraminifera): it may not be possible to remove the volume that has received an external alpha dosage. Alpha and beta attenuation has to be considered. For the alpha attenuation of grains see Bell (1980), for layers see Aitken (1987) and Grün (1987). The following results have to be reported:

- U, Th, K and water contents of the sample
- U-series disequilibria (i.e. $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$)
- α -efficiency
- alpha self-irradiation
- beta self-irradiation
- external beta and alpha dose rate (U, Th, K and water of the immediate surroundings)
- alpha attenuation
- beta attenuation
- external gamma dose rate
- cosmic dose rate

For very small samples, such as foraminifera, it may be assumed that the alpha dose rate corresponds more or less to the infinite matrix dose (including the samples, see Mudelsee et al. 1992). In other cases, e.g. small quartz grains, this may not be valid.

These lists show the parameters that have to be cited in principle, but they may not necessarily apply to each dating approach. For example, one can estimate the external beta dose rate by (i) measuring U, Th, K of the immediate surrounding using neutron activation analysis and the water content or by (ii) measuring the beta activity of the immediate surroundings with, for example, a thick source beta counter, TSBC (see Sanderson 1988) and the water content. Each approach has its own merits. In order to measure attenuation factors, the dimensions of the sample have to be measured and account taken of any layers that have been removed during sample preparation.

Errors in D determination

The exact error calculation for the total dose rate is rather complex. It is easily possible to estimate the errors for the analytical techniques, since they are usually based on counting statistics. Other sources of errors, however, are rather difficult to estimate, such as the average water content in the sediment. One solution seems to be measurement of the present day water content and to assume a relative large error (e.g. $10 \pm 5\%$ by weight). Berger (1988) suggests to measure the present saturation water content and derive the average water concentration and error from the in situ water content and site information. As long as no U-series disequilibria are involved in the age calculation, Appendix B of Aitken (1985) deals extensively with the error calculation of TL (and hence ESR) age estimates. Since the formulae for U-series disequilibria are rather lengthy (see e.g. Grün 1989) it seems technically simpler to estimate the influence of each uncertainty on the calculation of the total dose rate. This approach is valid as long as the error is approximately linear and corresponds to a numerical derivation. The total error results from the square root of the sum of squares of the individual error contributions.

Some parameters whose occurrence is rather uncertain, such as Rn loss or U-series disequilibria in sediments, should only be included in the estimation of the dose rate if they have actually been measured. Otherwise, readers may get the impression that the introduction of those processes was used to arrive at a convenient result! In practice, most of the general information can be given in the foot note of a table.

I wish to emphasise that at present the points outlined above may be regarded as a basis for discussion. I hope that many further suggestions will be made to improve these suggestions and to establish firm requirements for

the citations of ESR age estimates prior to the next International Seminar on TL and ESR Dating in Vienna in 1993.

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