Pergamon

PII S0016-7037(97)00130-0

SCIENTIFIC COMMENT

Propagating errors in decay equations: Examples from the Re-Os isotopic system

MALCOLM SAMBRIDGE[1] and DAVID D. LAMBERT[2]

[1]Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia
[2]Victorian Institute of Earth and Planetary Sciences, Department of Earth Sciences, Monash University, Clayton, Victoria 3168, Australia

Abstract—Statistical evaluation of radiogenic isotope data commonly makes use of the isochron method to determine closure age and initial isotopic composition which can be related to the source region from which the rocks or minerals were derived. Isochron regression algorithms also yield estimates of uncertainties in age and initial isotopic composition. However, geochemists frequently require an estimate of uncertainties associated with the calculation of initial isotopic composition and model age for single samples. This is often the case with Re-Os isotopic data for small sample suites that may not be isochronous. Here we describe two methods of propagating errors associated with Re-Os isotopic measurements in order to estimate uncertainties associated with both of these geologically important parameters; however, these methods are equally applicable to other isotopic systems. The first result is a set of analytical formulae that provide error estimates on both variables, even for the most general case where all dependent variables contain error, and all pairs of variables are correlated. This numerical approach leads to equations that can be easily and efficiently evaluated. A second Monte Carlo procedure was initially implemented to check the accuracy of the analytical formulae, although in the cases tested here it has also proved to be efficient and may even be practical for routine use. The advantage of error analysis of this type is that we can assign a level of confidence and thus significance to calculated initial isotopic compositions and model ages, especially for Archean rocks. *Copyright © 1997 Elsevier Science Ltd*

1. INTRODUCTION

The rhenium (Re)-osmium (Os) isotopic system, based on the beta decay of ^{187}Re to ^{187}Os with a decay constant of $1.64 \pm 0.05 \times 10^{-11}$ yr^{-1} (Lindner et al., 1989), is a relatively new and powerful tracer of global geochemical processes (Allégre and Luck, 1980). This property stems from the fact that Re behaves incompatibly during mantle melting and crust formation (Morgan et al., 1981), whereas Os is retained in olivine, sulfide, and/or metal alloy phases in refractory mantle residues (Mitchell and Keays, 1981; Morgan et al., 1981; Morgan, 1986). This geochemical difference results in terrestrial reservoirs with dramatically different Re/Os ratios and with time, very different Os isotopic compositions (Allégre and Luck, 1980). For reference, carbonaceous chondrites have ^{187}Re/^{188}Os of 0.401 and a present-day ^{187}Os/^{188}Os averaging 0.1271 (Walker and Morgan, 1989), the latter value closely matching that of the asthenospheric upper mantle source of midocean ridge basalts (DMM source: Martin and Turekian, 1987; Martin, 1991; Snow et al., 1991; Snow and Reisberg, 1995). This contrasts with estimates of ^{187}Re/^{188}Os and ^{187}Os/^{188}Os in the upper crust of 42 and 1.69, respectively (Esser and Turekian, 1993). No other radiogenic isotope system shows this extreme geochemical and isotopic contrast between crustal and mantle reservoirs.

To extend the modern Os isotopic database and to constrain the temporal evolution of Os in the DMM and other reservoirs that are isotopically distinct in Sr, Nd, and Pb

isotope geochemistry (e.g., EM1, EM2 and HIMU; Zindler and Hart, 1986; Hauri and Hart, 1993) requires that precise and accurate initial Os isotopic compositions be produced for nonzero age rocks. As in other radiogenic isotope systems, there are two ways of achieving this aim: (1) graphically using an isochron diagram of measured ^{187}Re/^{188}Os plotted vs. measured ^{187}Os/^{188}Os for a suite of cogenetic rocks, or (2) calculating an initial Os isotopic composition for a single rock or mineral analysis using measured ^{187}Re/^{188}Os and ^{187}Os/^{188}Os and independent geochronological constraints. The isochron method is preferred because this technique permits the geochemist to assess "closed-system" isotopic behavior and yields estimates of the closure age, initial Os isotopic composition, and errors associated with these two parameters via regression algorithms (e.g., Brooks et al., 1972; McIntyre et al., 1966; York, 1967, 1969). Using method 2, error propagation becomes an acute problem when assessing published Re-Os isotopic data for Precambrian rocks that have high Re/Os ratios (e.g., most mantle- and crustally-derived melts and sediments), as the error in calculated initial Os isotopic composition is a combined and propagated function of analytical errors in measured ^{187}Re/^{188}Os and ^{187}Os/^{188}Os, decay constant, and age of the rock. Walker et al. (1994) investigated error propagation (assuming constant uncertainties in ^{187}Re/^{188}Os and ^{187}Os/^{188}Os) applicable to rocks with an age of 246 Ma, but no generally applicable statistical analysis of error propagation for rocks of any age has been attempted until now.

A second geochemical parameter that is often uncon-

strained by rigorous error analysis is the chondritic-mantle model age (represented in this paper as t_{CH}) in which measured $^{187}Os/^{188}Os$ is age corrected using measured $^{187}Re/^{188}Os$ until $^{187}Os/^{188}Os$ of the sample intersects a carbonaceous chondrite Os isotopic growth line (Allégre and Luck, 1980). The Os t_{CH} model age is analogous to the Nd t_{DM} model age in that the Earth's DMM reservoir has been shown to be near-chondritic (within 3%) in Re-Os isotope geochemistry (Martin and Turekian, 1987; Martin, 1991; Snow et al., 1991; Snow and Reisberg, 1995). Thus, these model ages approximate the time of fractionation and separation of Os and Nd in the sample from Os and Nd in a depleted mantle (DMM) reservoir. Using this approach, Os and Nd model ages can yield useful estimates of mantle extraction or "crustal residence times" for an igneous source, metamorphic protolith, or sediment provenance. However, for t_{CH} to have geological significance, one must assume that measured $(^{187}Re/^{188}Os)_{rock} = (^{187}Re/^{188}Os)_{source}$, which in many cases, is difficult to justify because Re is believed to be less compatible than Os during mantle and crustal melting processes (Morgan et al., 1981). Moreover, the model mantle parameters used in both Re-Os and Sm-Nd isotopic studies only approximate the geochemistry of the convecting upper mantle of the Earth. Thus, Os t_{CH} model ages are *minimum* crustal residence times, as are Nd t_{DM} model ages. Because of this, rigorous error estimation for these parameters is not as easily justified as is the case for initial Os and Nd isotopic compositions which are frequently used to constrain the geochemical characteristics of the Precambrian mantle (e.g., Bennett and Esat, 1995; Foster et al., 1996; Shirey and Walker, 1994).

In this paper we present two approaches for estimating how errors propagate into the initial Os isotopic composition, $(^{187}Os/^{188}Os)_i$, and the chondritic-mantle model age, t_{CH}, through the ^{187}Re-^{187}Os decay equation. It is our intention that the paper take on a 'tutorial flavour,' enabling readers to use the methodology presented here on their own datasets. The first method is entirely analytical and results in a set of convenient formulae for calculating the standard error in both variables, given standard errors in all other variables. These formulae can be implemented in standard spread sheets used in data reduction and can be applied to other isotopic systems (e.g., Rb-Sr, Sm-Nd, Lu-Hf) with a change in model parameters and decay constants. The second approach is entirely numerical, and allows error estimates to be generated with any degree of precision. The primary reason for using the second approach is to test the accuracy of the first, however, it is very efficient and in many cases may be practical for routine use.

2. DEFINITIONS AND THEORY

The error analysis is based on the following two equations:

$$\left(\frac{^{187}Os}{^{188}Os}\right)_i = \left(\frac{^{187}Os}{^{188}Os}\right)_{rock} - \left(\frac{^{187}Re}{^{188}Os}\right)_{rock}(e^{\lambda t} - 1) \quad (1)$$

$$t_{CH} = \frac{1}{\lambda}\ln\left[1 + \frac{((^{187}Os/^{188}Os)_{rock} - (^{187}Os/^{188}Os)_{mantle})}{((^{187}Re/^{188}Os)_{rock} - (^{187}Re/^{188}Os)_{mantle})}\right] \quad (2)$$

where $(^{187}Os/^{188}Os)_{rock}$ is an atomic ratio measured via a technique such as negative-thermal ionization mass spectrometry (N-TIMS) and is usually precise at the 0.1–1% level of uncertainty (2 standard errors of the mean, in-run statistics). $(^{187}Re/^{188}Os)_{rock}$ is calculated based on measured Re and Os abundances and isotopic composition as determined by isotope dilution N-TIMS and is usually accurate at the 1–5% level of uncertainty, primarily because of problems associated with Os spike calibration (see Morgan et al., 1995). $(^{187}Os/^{188}Os)_i$ is the initial Os isotopic composition that can be calculated for a single sample using the crystallization age of the rock (t), the ^{187}Re decay constant (λ), and Eqn. 1. Currently, the ^{187}Re decay constant is known to only approximately ±3% (Lindner et al., 1989), and the uncertainty in age is highly variable depending on the independent dating method used (e.g., U-Pb zircon ages can have uncertainties of <0.5% at 2700 Ma, whereas Rb-Sr and Sm-Nd isochron ages can have uncertainties of >1% at 2700 Ma). In this paper, $(^{187}Re/^{188}Os)_{mantle}$ and $(^{187}Os/^{188}Os)_{mantle}$ are carbonaceous chondrite atomic ratios from Walker and Morgan (1989) that closely approximate these same parameters in the DMM reservoir of the Earth. No uncertainties have been included for these two parameters, as they are representative only of a model terrestrial reservoir. In practice, readers may insert whatever model parameters they prefer. The parameter, t_{CH}, is the chondritic-mantle model age that can be calculated for a single sample using Eqn. 2. For ease of notation we will replace the five isotopic ratios with the following symbols,

$$r = \left(\frac{^{187}Os}{^{188}Os}\right)_i, \ r_1 = \left(\frac{^{187}Os}{^{188}Os}\right)_{rock}, \ r_2 = \left(\frac{^{187}Re}{^{188}Os}\right)_{rock}$$

$$r_3 = \left(\frac{^{187}Os}{^{188}Os}\right)_{mantle}, \ r_4 = \left(\frac{^{187}Re}{^{188}Os}\right)_{mantle} \quad (3)$$

Using these we can rewrite Eqns. 1 and 2 in the simpler form,

$$r = r_1 - r_2(e^{\lambda t} - 1) \quad (4)$$

$$t_{CH} = \frac{1}{\lambda}\ln\left[1 + \frac{(r_1 - r_3)}{(r_2 - r_4)}\right] \quad (5)$$

where all variables except r_3 and r_4 on the right-hand side of Eqns. 4 and 5 are assumed to contain error and we wish to find the resulting standard errors in the variables r and t_{CH}. The nature of the errors on any variable, say r_1, is provided by its probability density function (PDF). In many cases these are assumed to be Gaussian, although they may take other forms (see Meyer, 1965).

Note that we do not consider errors of a systematic nature, e.g., those which might arise from the inappropriateness of the model equations, 4 and 5. Usually these "theory errors" can only be taken into account if they have a well known, and usually simple form (see Tarantola, 1987, for an example). In this paper, we deal only with error propagation from the input variables, i.e., those on the right-hand side of Eqns. 4 and 5, $(r_1, r_2, r_3, r_4, \lambda, t)$, to the output variables, i.e., those on the left-hand side of 4 and 5, (r, t_{CH}), assuming that the model equations are "error free." We will assume that all six input variables have known measured values

(denoted by η_1, η_2, η_3, η_4, η_λ, η_t) and standard errors (denoted by σ_1, σ_2, σ_3, σ_4, σ_λ, σ_t). The object is then to find the means (η_r, $\eta_{t_{CH}}$) and standard deviations (σ_r, $\sigma_{t_{CH}}$) of the initial isotopic composition, r, and chondritic-mantle model age, t_{CH}. We present two alternative methods to solve this problem, each with its own advantages.

2.1. Method 1: Analytical Formulae

The first approach is to derive analytical formulae for the means and standard deviations of the output variables, r and t_{CH}. From Eqn. 4 we can see that r depends on four variables (r_1, r_2, λ, t), while t_{CH} depends on five variables (r_1, r_2, r_3, r_4, λ). Because Eqns. 4 and 5 are nontrivial, the PDFs of r and t_{CH} are in general unknown, even if the PDFs of the original variables are simple. However, estimates of their means and standard deviations can be found without first finding the PDFs.

To demonstrate the general procedure consider the simpler case when an unknown g, is dependent on only two random variables x and y, with mean values (η_x, η_y) and standard deviations (σ_x, σ_y). In this case it can be shown (see, e.g., Papoulis, 1991) that if the function $g(x, y)$ varies sufficiently smoothly about the mean values (η_x, η_y), then estimates of the mean, η_g, and standard deviation, σ_g, of g are given by

$$\eta_g = g(\eta_x, \eta_y)$$
$$+ \frac{1}{2}\left[\left(\frac{\partial^2 g}{\partial x^2}\right)\sigma_x^2 + 2C\left(\frac{\partial^2 g}{\partial x \partial y}\right)\sigma_x\sigma_y + \left(\frac{\partial^2 g}{\partial y^2}\right)\sigma_y^2\right] \quad (6)$$

$$\sigma_g^2 = \left(\frac{\partial g}{\partial x}\right)^2\sigma_x^2 + 2C\left(\frac{\partial g}{\partial x}\right)\left(\frac{\partial g}{\partial y}\right)\sigma_x\sigma_y + \left(\frac{\partial g}{\partial y}\right)^2\sigma_y^2 \quad (7)$$

where all derivatives are evaluated at (η_x, η_y) and C is the correlation coefficient of the variables x and y (see the Appendix). Equation 6 gives an estimate of how much the mean of g varies from the "calculated value" $g(\eta_x, \eta_y)$, which indicates the degree of skewness of the PDF of g. Equation 7 shows how errors propagate from the variables x and y to the variable g.

The two variable cases can be extended to any number of variables and applied to Eqns. 4 and 5. In the case of the initial Os isotopic composition, r, we obtain

$$\eta_r = r_0 - \frac{1}{2}(\eta_t^2\sigma_\lambda^2 + \eta_\lambda^2\sigma_t^2)\eta_2 e^{\eta_\lambda\eta_t} \quad (8)$$

$$\sigma_r^2 = \sigma_1^2 + (1 - e^{\eta_\lambda\eta_t})^2\sigma_2^2 + (\eta_t^2\sigma_\lambda^2 + \eta_\lambda^2\sigma_t^2)\eta_2^2 e^{2\eta_\lambda\eta_t} \quad (9)$$

where r_0 is the value of the initial isotopic composition found from Eqn. 4, and we have assumed that all variables are uncorrelated (so that all correlation coefficients are zero). If any pair of the variables (r_1, r_2, λ, t) are correlated, then extra terms need to be added to Eqns. 8 and 9. Full details of these extra terms are contained in the Appendix. Even though the equations look complicated, they are easily evaluated because all terms on the right-hand side are merely functions of original variables and their estimated errors, all of which are known in advance. If we apply the same approach to the chondritic-mantle model age in Eqn. 5 (again assuming un-correlated errors), we obtain an estimate of the mean value of t_{CH}

$\eta_{t_{CH}}$

$$= t_0 + \frac{1}{2}[g_1''\sigma_1^2 + g_2''\sigma_2^2 + g_3''\sigma_3^2 + g_4''\sigma_4^2 + g_\lambda''\sigma_\lambda^2] \quad (10)$$

where

$$g_1'' = g_3'' = \frac{-1}{\eta_\lambda(\eta_1 + \eta_2 - \eta_3 - \eta_4)^2} \quad (11)$$

$$g_2'' = g_4'' = \frac{2(\eta_1 - \eta_3)[2(\eta_2 - \eta_4) + \eta_1 - \eta_3]}{\eta_\lambda(\eta_2 - \eta_4)^2(\eta_1 + \eta_2 - \eta_3 - \eta_4)^2} \quad (12)$$

$$g_\lambda'' = \frac{2t_0}{\eta_\lambda^2} \quad (13)$$

In Eqn. 10 t_0 is the value of the chondritic-mantle model age evaluated from Eqn. 5. If we extend Eqn. 7 to five variables and apply it to Eqn. 5, we obtain an estimate for the standard deviation of t_{CH}

$$\sigma_{t_{CH}}^2 = (g_1')^2\sigma_1^2 + (g_2')^2\sigma_2^2 + (g_3')^2\sigma_3^2$$
$$+ (g_4')^2\sigma_4^2 + (g_\lambda')^2\sigma_\lambda^2 \quad (14)$$

where

$$g_1' = -g_3' = \frac{1}{\eta_\lambda(\eta_1 + \eta_2 - \eta_3 - \eta_4)} \quad (15)$$

$$g_2' = -g_4' = \frac{(\eta_3 - \eta_1)}{\eta_\lambda(\eta_2 - \eta_4)(\eta_1 + \eta_2 - \eta_3 - \eta_4)} \quad (16)$$

$$g_\lambda' = \frac{-t_0}{\eta_\lambda} \quad (17)$$

If the coefficient of correlation of any pair of variables is nonzero, then extra terms must also be added to Eqns. 10 and 14; again, these are given in the Appendix. In practice, Eqns. 9 and 14 will be easy to evaluate and provide a direct estimate of how errors are propagated into r and t_{CH}.

2.2. Method 2: Monte Carlo Simulation

Because the analytical approach described above uses approximations, we do not know how accurate the error estimates are likely to be in practice. To gain some insight we use a second method, known as a Monte Carlo simulation, to estimate both the mean and standard deviation of the two dependent variables, r and t_{CH}. A Monte Carlo simulation has "tunable" accuracy, which means that a more accurate result can be achieved simply by increasing the number of random trials used in the procedure. It may therefore be used to test the accuracy of the analytical procedure.

Monte Carlo simulation is a well known, powerful technique for problems of this kind and is used in many areas of statistics (see Press et al., 1992). In the case of the isotopic ratio, r, we randomly generate errors for each of the input variables (r_1, r_2, λ, t) according to their known PDF, add these to the mean values (η_1, η_2, η_λ, η_t), and evaluate the output value using Eqn. 4. When this process is repeated many times, a histogram of the output values will approximate its PDF, while the mean and standard deviation will approximate the required mean and standard deviation, (σ_r, s_r). A similar procedure can be applied to the model age,

t_{CH}, using Eqn. 5. The accuracy of this approach depends on the number of times the process is repeated. Usually many thousands of repeated trials are required, but the important point is that we can always increase the number of trials if more accurate results are needed.

Standard numerical procedures exist for generating errors according to a Gaussian, or any other known PDF (see Press et al., 1992). For the particular case in which the errors on input variables are Gaussian and uncorrelated, the errors on each parameter may be generated independently. Technically, this is because the principal axes of the joint PDF are aligned with the parameter space axes. The more general correlated error case occurs when the principal axes of the joint PDF (eigen-vectors of the covariance matrix) are inclined to the parameter space axes. Therefore, correlated errors may be generated by first generating errors independently and then rotating the parameter space axes. The level of rotation determines the amount of correlation one may wish to introduce. The analytical formulae can take account of correlated errors using the extension described in the Appendix. In our illustration of the Monte Carlo procedure we will assume uncorrelated errors and use the simple approach in Press et al. (1992).

3. APPLICATION TO A SYNTHETIC RE-OS ISOTOPIC DATASET

To test the two approaches we used the following typical values for the input variables and errors: $(^{187}Os/^{188}Os)_{rock}$ = (10, ± 0.025), $(^{187}Re/^{188}Os)_{rock}$ = (200, ± 1.0), $(^{187}Re/^{188}Os)_{mantle}$ = (0.40076, ± 0), $(^{187}Os/^{188}Os)_{mantle}$ = (0.1271, ± 0), decay constant λ = (1.64 × 10^{-11} yr^{-1}, ±2.46 × 10^{-13} yr^{-1}), and age, t, = (2.7 × 10^9 yr, ± 1.35 × 10^7 yr). Using these values in Eqns. 4 and 5, we obtain a value of 0.945 for the initial isotopic ratio at 2.7 Ga, r, and 2.94 Ga for the chondritic-mantle model age, t_{CH}. For the analytical method, we obtain (0.9450, ± 0.1552) and (2.9446 Ga, ± 0.047 Ga) for these two parameters, while the Monte Carlo simulation gave (0.9454 ± 0.1555) and (2.9445 Ga, ± 0.0475 Ga). The latter was based on 10^5 repeated trials and took less than 4 sec on a Sun Sparc 5 workstation. The two methods are clearly in good agreement, which indicates that both the number of trials in the Monte Carlo procedure are large enough and that the approximate formulae given by Eqns. 8, 9, 10, and 14 are sufficiently accurate. The Monte Carlo simulations also showed a near perfect Gaussian distribution of output values which indicates that the non-linearity of the decay equations is not too severe for the error analysis.

Figure 1 illustrates how errors propagate through time in the calculation of initial $^{187}Os/^{188}Os$ for rocks and minerals with $^{187}Re/^{188}Os$ ratios of 1-200. Note that uncertainties are large (>1%) for old samples (>1000 Ma) with high $^{187}Re/$ ^{188}Os ratios (e.g., Archean crustal rocks). The figure thus illustrates the need to analyze rocks or minerals with low $^{187}Re/^{188}Os$ in order to minimize the errors associated with this calculation. High-degree partial melts of the mantle (e.g., komatiites and picrites) and mineral separates with low $^{187}Re/^{188}Os$ (e.g., chromite) are desirable materials in this regard and have been used to trace mantle source characteristics for Archean rocks (Bennett and Esat, 1995; Foster
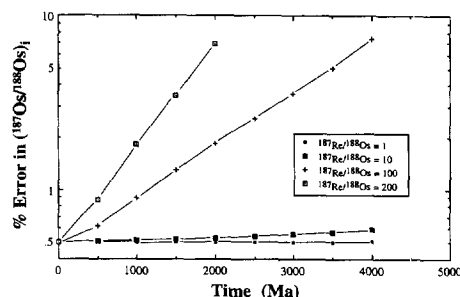

Fig. 1. Error in initial Os isotopic composition (in %) vs. time diagram, illustrating how errors propagate and expand as a function of age of the sample and $^{187}Re/^{188}Os$ ratio. The four curves correspond to $^{187}Re/^{188}Os$ ratios of 1, 10, 100, and 200, appropriate for high-degree mantle melts such as komatiites and chromite mineral separates (1) to low-degree mantle melts such as basalts and crustal materials such as sediments and granites (100-200). The curves were calculated assuming constant uncertainty in measured $^{187}Os/$ ^{188}Os (0.5% two-sigma) and measured $^{187}Re/^{188}Os$ (1% two-sigma), a 1% uncertainty in age, and a 3% uncertainty in the ^{187}Re decay constant. Note that uncertainties are large (>1%) for old samples (>1000 Ma) with high $^{187}Re/^{188}Os$ ratios (e.g., Archean crustal rocks).

et al., 1996; Lambert et al., 1994; Walker et al., 1988). However, in practice, the error in measured $^{187}Os/^{188}Os$ is not constant at 0.5% (two-sigma), as was assumed in the construction of Fig. 1, but can increase with increasing $^{187}Re/$ ^{188}Os due to lower Os abundances. Hence, lower precision mass spectrometer data (usually limited by counting statistics) results in errors that are larger than would be predicted by Fig. 1.

4. CONCLUSIONS

We have presented two methods for calculating how errors propagate into the initial isotopic ratio, $(^{187}Os/^{188}Os)_i$, and the chondritic-mantle model age, t_{CH}, through the isotopic decay Eqns. 1 and 2. The result is a set of analytical formulae that provide error estimates on both variables, even for the most general case where all dependent variables contain error and all pairs of variables are correlated. The expressions may be easily and efficiently evaluated. The Monte Carlo procedure was initially implemented merely to check the accuracy of the analytical formulae, although in the cases tested here it has also proved to be efficient and may even be practical for routine use. The advantage of the error analysis methods derived in this paper is that we can assign a level of confidence and thus significance to calculated initial Os isotopic compositions and chondritic-mantle model ages, especially for Archean rocks.

Editorial handling: K. R. Ludwig

REFERENCES

Allégre C. J. and Luck J.-M. (1980) Osmium isotopes as petrogenetic and geological tracers. *Earth Planet. Sci. Lett.* **48**, 148–154.

Bennett V. C. and Esat T. M. (1995) The osmium isotopic composition of the early Archean mantle. *Trans. Amer. Geophys. Union* **76**, S45.

Brooks C., Hart S. R., and Wendt I. (1972) Realistic use of two-error regression treatments as applied to rubidium-strontium data. *Rev. Geophys. Space Phys.* **10**, 551–577.

Esser B. K. and Turekian K. K. (1993) The osmium isotopic composition of the continental crust. *Geochim. Cosmochim. Acta* **57**, 3093–3104.

Foster J. G., Lambert D. D., Frick L. R., and Maas R. (1996) Re-Os isotopic evidence for genesis of Archaean nickel ores from uncontaminated komatiites. *Nature* **382**, 703–706.

Hauri E. K. and Hart S. R. (1993) Re-Os isotope systematics of HIMU and EMII oceanic island basalts from the south Pacific Ocean. *Earth Planet. Sci. Lett.* **114**, 353–371.

Lambert D. D. et al. (1994) Re-Os and Sm-Nd isotope geochemistry of the Stillwater Complex, Montana: Implications for the petrogenesis of the J-M Reef. *J. Petrol.* **35**, 1717–1753.

Lindner M., Leitch D. A., Russ G. P., Bazan J. M., and Borg R. J. (1989) Direct determination of the half-life of ^{187}Re. *Geochim. Cosmochim. Acta* **53**, 1597–1606.

Martin C. E. (1991) Osmium isotopic characteristics of mantle-derived rocks. *Geochim. Cosmochim. Acta* **55**, 1421–1434.

Martin C. E. and Turekian K. K. (1987) Osmium isotope systematics in abyssal peridotites: Implications for mantle evolution. *Geol. Soc. Amer. Abstr. Prog.* **19**, 761.

McIntyre G. A., Brooks C., Compston W., and Turek A. (1966) The statistical assessment of Rb-Sr isochrons. *J. Geophys. Res.* **71**, 5459–5468.

Meyer P. L. (1965) *Introductory Probability and Statistical Applications.* Addison-Wesley.

Mitchell R. H. and Keays R. R. (1981) Abundance and distribution of gold, palladium, and iridium in some spinel and garnet lherzolites: Implications for the nature and origin of precious metal-rich intergranular components in the upper mantle. *Geochim. Cosmochim. Acta* **45**, 2425–2442.

Morgan J. W. (1986) Ultramafic xenoliths: Clues to the Earth's late accretionary history. *J. Geophys. Res.* **91**, 12375–12387.

Morgan J. W., Wandless G. A., Petrie R. K., and Irving A. J. (1981) Composition of the Earth's upper mantle—I. Siderophile trace elements in upper mantle nodules. *Tectonophysics* **75**, 47–67.

Morgan J. W., Horan M. F., Walker R. J., and Grossman J. N. (1995) Rhenium-osmium concentration and isotope systematics in group IIAB iron meteorites. *Geochim. Cosmochim. Acta* **59**, 2331–2344.

Papoulis A. (1991) *Probability, Random Variables and Stochastic Processes,* 3d ed. McGraw-Hill.

Press W. H., Teukolsky S. A., Vetterling W. T., and Flannery B. P. (1992) *Numerical Recipes in FORTRAN: The Art of Scientific Computing,* 2d edn. Cambridge University Press.

Shirey S. B. and Walker R. J. (1994) Re-Os isotopic evidence for evolution of the source of ultramafic magmatism, Archean to the present. *Trans. Amer. Geophys. Union* **75**, 690.

Snow J. E. and Reisberg L. (1995) Os isotopic systematics of the MORB mantle: Results from altered abyssal peridotites. *Earth Planet. Sci. Lett.* **133**, 411–421.

Snow J. E., Hart S. R., and Dick H. J. B. (1991) Os isotopic composition of the oceanic upper mantle. *Trans. Amer. Geophys. Union* **72**, 527.

Tarantola A. (1987) *Inverse Problem Theory.* Elsevier.

Walker R. J. and Morgan J. W. (1989) Rhenium-osmium systematics of carbonaceous chondrites. *Science* **243**, 519–522.

Walker R. J., Shirey S. B., and Stecher O. (1988) Comparative Re-Os, Sm-Nd and Rb-Sr isotope and trace element systematics for Archean komatiite flows from Munro Township, Abitibi Belt, Ontario. *Earth Planet. Sci. Lett.* **87**, 1–12.

Walker R. J. et al. (1994) Re-Os isotopic evidence for an enriched-mantle plume source for the Noril'sk-type ore-bearing intrusions, Siberia. *Geochim. Cosmochim. Acta* **58**, 4179–4198.

York D. (1967) The best isochron. *Earth Planet. Sci. Lett.* **2**, 479–482.

York D. (1969) Least squares fitting of a straight line with correlated errors. *Earth Planet. Sci. Lett.* **5**, 320–324.

Zindler A. and Hart S. R. (1986) Chemical geodynamics. *Ann. Rev. Earth Planet. Sci.* **14**, 493–571.

APPENDIX

A.1. The Effect of Correlated Variables

If any pair of input variables are correlated then extra terms must be added to Eqns. 8, 9, 10, and 14. In the most general case of all pairs of variables being correlated, the extra terms which appear on the right-hand side of equation (8) are

$$-[C_{2,\lambda}\eta_t\sigma_2\sigma_\lambda + C_{2,t}\eta_\lambda\sigma_2\sigma_t + C_{\lambda,t}\eta_2\sigma_\lambda\sigma_t]e^{\eta_\lambda\eta_t} \quad (A1)$$

where $C_{2,\lambda}$ is the correlation coefficient between parameters r_2 and λ, and all other coefficients are expressed similarly. (For details on how to calculate correlation coefficients, see below.) For Eqn. 9, the extra terms on the right-hand side are

$$2[C_{1,2}\sigma_1\sigma_2(1 - e^{\eta_\lambda\eta_t})$$
$$- C_{2,\lambda}\sigma_2\sigma_\lambda(1 - e^{\eta_\lambda\eta_t})\eta_2\eta_t e^{\eta_\lambda\eta_t} - C_{1,\lambda}\sigma_1\sigma_\lambda(\eta_t\eta_2 e^{\eta_\lambda\eta_t})$$
$$- C_{1,t}\sigma_1\sigma_t(\eta_\lambda\eta_2 e^{\eta_\lambda\eta_t}) - C_{2,t}\sigma_2\sigma_t(1 - e^{\eta_\lambda\eta_t})\eta_2\eta_\lambda e^{\eta_\lambda\eta_t}$$
$$+ C_{\lambda,t}\sigma_\lambda\sigma_t(\eta_2^2\eta_\lambda\eta_t e^{2\eta_\lambda\eta_t})] \quad (A2)$$

For Eqn. 10, the extra terms are

$$[C_{1,2}\sigma_1\sigma_2 g_{1,2}'' + C_{1,3}\sigma_1\sigma_3 g_{1,3}''$$
$$+ C_{1,4}\sigma_1\sigma_4 g_{1,4}'' + C_{1,\lambda}\sigma_1\sigma_\lambda g_{1,\lambda}'' + C_{2,3}\sigma_2\sigma_3 g_{2,3}''$$
$$+ C_{2,4}\sigma_2\sigma_4 g_{2,4}'' + C_{2,\lambda}\sigma_2\sigma_\lambda g_{2,\lambda}'' + C_{3,4}\sigma_3\sigma_4 g_{3,4}''$$
$$+ C_{3,\lambda}\sigma_3\sigma_\lambda g_{3,\lambda}'' + C_{4,\lambda}\sigma_4\sigma_\lambda g_{4,\lambda}''], \quad (A3)$$

where

$$g_{1,2}'' = g_{3,4}'' = -g_{1,4}'' = -g_{2,3}''$$
$$= \frac{-1}{\eta_\lambda(\eta_1 + \eta_2 - \eta_3 - \eta_4)^2} \quad (A4)$$

$$g_{1,\lambda}'' = \frac{-1}{\eta_\lambda^2(\eta_1 + \eta_2 - \eta_3 - \eta_4)} \quad (A5)$$

$$g_{2,\lambda}'' = -g_{4,\lambda}'' = \frac{(\eta_1 - \eta_3)}{\eta_\lambda^2(\eta_2 - \eta_4)(\eta_1 + \eta_2 - \eta_3 - \eta_4)} \quad (A6)$$

In addition $g_{1,3}'' = -g_1''$ and $g_{2,4}'' = -g_2''$ can be evaluated using Eqns. 11 and 12. For Eqn. 14, the extra terms are

$$2[C_{1,2}\sigma_1\sigma_2 g_1' g_2' + C_{1,3}\sigma_1\sigma_3 g_1' g_3'$$
$$+ C_{1,4}\sigma_1\sigma_4 g_1' g_4' + C_{1,\lambda}\sigma_1\sigma_\lambda g_1' g_\lambda' + C_{2,3}\sigma_2\sigma_3 g_2' g_3'$$
$$+ C_{2,4}\sigma_2\sigma_4 g_2' g_4' + C_{2,\lambda}\sigma_2\sigma_\lambda g_2' g_\lambda' + C_{3,4}\sigma_3\sigma_4 g_3' g_4'$$
$$+ C_{3,\lambda}\sigma_3\sigma_\lambda g_3' g_\lambda' + C_{4,\lambda}\sigma_4\sigma_\lambda g_4' g_\lambda'] \quad (A7)$$

where all first derivative terms, g_i' etc, are given by Eqns. 15 to 17. Again, these extra terms are simply functions of

the estimated value and standard deviation of each of the original variables, and can be evaluated without difficulty.

The calculation of correlation coefficients is a standard procedure in statistical analysis. A positive error correlation between two parameters indicates that to the extent that the measured value for one parameter is too high (or too low), the measured value for the other parameter will also tend to be too high (or too low). A negative error correlation implies the opposite. Usually a correlation coefficient between any two variables, say x and y, can be determined experimentally from a set of "measurements" of the pair of variables. If we assume that we have n measurements, $[(x_i, y_i)\ i = 1,$

..., $n]$, then the correlation coefficient between the two is defined as (see Papoulis, 1991),

$$C_{x,y} = \frac{1}{\sigma_x \sigma_y} \left[\frac{1}{n} \sum_{i=1}^{n} x_i y_i - \eta_x \eta_y \right] \quad \text{(A14)}$$

where, as above, (η_x, η_y) and (σ_x, σ_y) are, respectively, the means and standard deviations of the two sets of measurements. This simple expression may be used to find correlation coefficients for each pair of input variables. If $C_{x,y}$ is equal to zero, then the two parameters are completely uncorrelated. This is often assumed to be the case if no other information is available.