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A general inversion for end-member ratios in binary mixing systems

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[1] Binary mixing is one of the most common models used to explain variations in geochemical data. When the data being modeled are ratios of elements or isotopes, the mixtures follow hyperbolic trends with curvatures that depend on a cross-term representing the relative concentrations of the elements or isotopes under consideration in the mixing components. The inverse problem of estimating mixing components is difficult because of the cross-term in the hyperbolic equation, which requires the use of nonlinear methods to estimate the mixing parameters, and because the end-member ratio values are intrinsically underdetermined unless the mixing proportions of the samples are known a priori, which is not generally the case. I use maximum likelihood methods to address these issues and derive a general inversion for binary mixing model parameters from ratio-ratio data. I apply the method to synthetic test data and a global compilation of $^{230}Th/^{232}Th$ versus $^{87}Sr/^{86}Sr$ data from oceanic basalts and find that the concentration ratio parameter is well-constrained by the inversion while the end-member ratio estimates are strongly dependent on the initial guesses used to start the iterative solver, reflecting the underdetermined nature of the end-member positions on the mixing hyperbola. Monte Carlo methods that randomly perturb the initial guesses can be used to improve error estimates, and goodness-of-fit statistics can be used to assess the performance of the mixing model for explaining data variance.

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1. Introduction

[2] Ratio-ratio data (isotope or element) in binary mixing systems form hyperbolas that can be described as a function of five model parameters (two sets of x and y axis ratio values and a concentration ratio) that characterize the end-members in the mixing model [*Langmuir et al.*, 1978; *Vollmer*, 1976]. In principle, mixture data can be used to constrain the end-members. In practice, however, difficulties arise owing to the cross-term in the hyperbolic equation, which precludes formal linearization of the full inverse problem, and the fact that the positions of the end-members on the mixing hyperbola are intrinsically underdetermined.

[3] *Albarede* [1995, p. 262] addressed these problems by parameterizing the mixing hyperbola in terms of its curvature and asymptotes. This parameterization reduces the number of model parameters from five to three (the end-members are constrained by asymptotes rather than a complete set of x and y axis ratio values), and it allows for the application of linear least squares methods to estimate the model parameters. In many cases, however, it is not possible to address the scientific question(s) of interest with asymptotic limits, par-

ticularly if the curvature of the mixing trend is weak, in which case asymptotic constraints have little physical meaning.

[4] Forward methods are commonly used to circumvent the mathematical barriers to the inversion of ratio-ratio data. Mixing components can be inferred by fitting ratio-ratio data "by eye." This approach allows for the identification of plausible mixing models, but it does not provide an objective means to optimize the model fit to the data, nor does it provide a means to quantify the uncertainty of the model parameters. These considerations motivate the development of a general method for inverting mixture data to find "best-fitting" models and obtaining formal parameter uncertainty estimates.

[5] In this paper I present a method for inverting ratio-ratio data to generate estimates of the five general mixing parameters (two sets of x and y axis ratio values and concentration ratio). I derive the gradient matrix relating the data to the mixing model parameters, and use a nonlinear, maximum likelihood method to minimize the misfit from a starting model. I apply the method to synthetic test data and to $^{230}Th/^{232}Th$ versus $^{87}Sr/^{86}Sr$ data from oceanic basalts to demonstrate practical aspects of implementation.

2. Method

[6] The general equation for the binary (i.e., two-component) mixing hyperbola in ratio-ratio coordinates as derived by *Vollmer* [1976] is

$$Ax + Bxy + Cy + D = 0, \tag{1}$$

where

$$\begin{aligned} A &= a_2b_1Y_2 - a_1b_2Y_1 \\ B &= a_1b_2 - a_2b_1 \\ C &= a_2b_1X_1 - a_1b_2X_2 \\ d &= a_1b_2X_2Y_1 - a_2b_1X_1Y_2 \end{aligned} \tag{2}$$

and

X_i x axis ratio of component i (e.g., $^{87}Sr/^{86}Sr$);
Y_i y axis ratio of component i (e.g., $^{143}Nd/^{144}Nd$);
a_i concentration of denominator of Y_i (e.g., $^{144}Nd_i$);
b_i concentration of denominator of X_i (e.g., $^{86}Sr_i$).

[11] The curvature of the hyperbola is controlled by the concentration ratio

$$c = {(a_1/b_1)}\Big/{(a_2/b_2)}, \tag{3}$$

which can be seen by making the substitution

$$a_1b_2 = ca_2b_1$$

into equations (1) and (2) and dividing by the common term a_2b_1, resulting in

$$f = A'x + B'xy + C'y + D' = 0, \tag{4}$$

where

$$\begin{aligned} A' &= Y_2 - Y_1c \\ B' &= c - 1 \\ C' &= X_1 - X_2c \\ D' &= Y_1X_2c - Y_2X_1 \end{aligned} \tag{5}$$

The mixing hyperbola is now an explicit function of five unknown parameters, X_1, X_2, Y_1, Y_2, and c, which define the isotope ratios and the concentration ratio of the end-members.

[12] To formulate the inverse problem I define the data and model row vectors, **d** and **m**, respectively, as

$$\mathbf{d} = [x_1, x_2, \ldots, x_N, y_1, y_2, \ldots, y_N]^T \tag{6}$$

and

$$\mathbf{m} = [X_1, X_2, Y_1, Y_2, c]^T, \tag{7}$$

where the data consist of N pairs of x-y ratio-ratio data (i.e., x_i is the x axis ratio of the ith observation). The relationship between **d** and **m** is nonlinear because of the cross term in equation (4).

[13] I group the data and model vectors into a single vector $\mathbf{z} = [\mathbf{d}, \mathbf{m}]$, which has $2N + 5$ rows and is defined as

$$\mathbf{z} = [x_1, x_2, \ldots, x_N, y_1, y_2, \ldots, y_N, X_1, X_2, Y_1, Y_2, c]^T. \tag{8}$$

The initial value of **z** is determined by the N ratio-ratio data pairs and initial guesses for the model parameters. Thus

$$\begin{aligned} \mathbf{z}_0 &= [\mathbf{d}, \mathbf{m}_0] \\ &= [x_1, x_2, \ldots, x_N, y_1, y_2, \ldots, y_N, X_{01}, X_{02}, Y_{01}, Y_{02}, c_0]^T, \end{aligned} \tag{9}$$

where the subscript "0" indicates an initial guess. Assuming that the data and model have Gaussian distributions, the prior distribution of $\mathbf{z}$ is

$$P_A(\mathbf{z}) \propto \exp\left[\left(-1/2\right)(\mathbf{z}-\mathbf{z}_0)^{\mathrm{T}}[\mathrm{cov}\ \mathbf{z}_0]^{-1}(\mathbf{z}-\mathbf{z}_0)\right], \quad (10)$$

where cov $\mathbf{z}_0$ is the prior covariance matrix. The objective of the minimization problem is to maximize (10) constraint to the mixing hyperbola equation (4). This is accomplished using Lagrange multipliers [*Menke*, 1989; *Tarantola and Valette*, 1982], leading to the iterative formula

$$\hat{\mathbf{z}}_{n+1} = \mathbf{z}_0 + [\mathrm{cov}\ \mathbf{z}_0]\mathbf{F}_n^{\mathrm{T}}\left(\mathbf{F}_n[\mathrm{cov}\ \mathbf{z}_0]\mathbf{F}_n^{\mathrm{T}}\right)^{-1} \cdot (\mathbf{F}_n[\hat{\mathbf{z}}_n - \mathbf{z}_0] - \mathrm{f}(\hat{\mathbf{z}}_n)), \quad (11)$$

where $\hat{\mathbf{z}}_n$ and $\mathrm{f}(\hat{\mathbf{z}}_n)$ are the values of $\mathbf{z}$ and equation (4) evaluated for the nth iteration, and $\mathbf{F}_n = \nabla \mathrm{f}(\hat{\mathbf{z}}_n)$ is a gradient matrix (a complete description of the nonlinear minimization technique is provided by *Sohn and Menke* [2002]).

[14] The gradient matrix has one row for each observation (data pair) and one column for each element of $\mathbf{z}$. F is thus $N \times (2N + 5)$, and has elements defined by

$$\mathbf{F}_{ij} = \frac{\partial F_i}{\partial \mathbf{z}_j} = \frac{\partial F_i}{\partial x_j} = (Y_2 - Y_1 c + (c-1)y_i)\delta(i,j) \quad \text{for } 1 \le j \le N \quad (12)$$

$$\mathbf{F}_{ij} = \frac{\partial F_i}{\partial \mathbf{z}_j} = \frac{\partial F_i}{\partial y_j} = ((c-1)x_i + X_1 - X_2 c)\delta(i, j-N) \quad \text{for } N+1 \le j \le 2N$$

$$\mathbf{F}_{ij} = \frac{\partial F_i}{\partial \mathbf{z}_j} = \frac{\partial F_i}{\partial X_1} = y_i - Y_2 \qquad \text{for } j = 2N+1$$

$$\mathbf{F}_{ij} = \frac{\partial F_i}{\partial \mathbf{z}_j} = \frac{\partial F_i}{\partial R_B^X} = c(Y_1 - y_i) \qquad \text{for } j = 2N+2$$

$$\mathbf{F}_{ij} = \frac{\partial F_i}{\partial \mathbf{z}_j} = \frac{\partial F_i}{\partial Y_1} = c(X_2 - x_i) \qquad \text{for } j = 2N+3$$

$$\mathbf{F}_{ij} = \frac{\partial F_i}{\partial \mathbf{z}_j} = \frac{\partial F_i}{\partial Y_2^Y} = x_i - X_1 \qquad \text{for } j = 2N+4$$

$$\mathbf{F}_{ij} = \frac{\partial F_i}{\partial \mathbf{z}_j} = \frac{\partial F_i}{\partial c} = x_i y_i - Y_1 x_i - X_2 y_i + Y_1 X_2 \quad \text{for } j = 2N+5$$

where $\delta(i, j)$ is the Kronecker delta function with the property

$$\delta(i,j) = 1 \qquad \text{for } i = j$$

$$\delta(i,j) = 0 \qquad \text{for } i \ne j$$

[15] The initial values are adjusted until convergence is achieved, at which point the parameter estimates, $\hat{m} = [\hat{X}_1, \hat{X}_2, \hat{Y}_1, \hat{Y}_2, \hat{c}]$, are generated. The inversion is considered to have converged once the difference between successive iterations, $d\mathbf{z}_{n+1} = |\mathbf{z}_{n+1} - \mathbf{z}_n|$, is below a specified threshold for all elements of $d\mathbf{z}$.

[16] Estimation of confidence intervals for the mixing model parameters is a difficult problem. Analytical expressions for model parameter uncertainty do not exist for nonlinear inverse problems, even if a Gaussian sampling distribution is assumed. Linear approximations, which multiply the prior covariance matrix by an operator formed with the last iteration of the gradient matrix, might be used if the problem is not too nonlinear [e.g., *Menke*, 1989], but nonparametric methods such as the bootstrap and jackknife, are preferred because they are insensitive to the linearity of the problem and the parameter sampling distributions.

[17] The problem of estimating uncertainties for the mixing model parameters is further complicated by the ill-posed nature of the inverse with respect to the end-member isotope ratio estimates. Conceptually, the problem arises from the fact that the position of the end-members on the mixing hyperbola is unconstrained by the data. In the absence of additional information there is no way of knowing how close the end-members sit with respect to the data field. This issue is discussed in some detail in section 3.1.

[18] A natural way to investigate the influence of the initial guesses on the parameter estimates is to repeat the inversion with a variety of initial values and examine the outcomes. This is conceptually similar to bootstrapping [*Efron*, 1987] except that it is the initial values, rather than the data, that are randomized for each repeat inversion. If a feasible range of isotope ratios for a given problem can be identified, then initial values can be drawn at random from within these intervals and bootstrap methods can be used to generate uncertainty estimates. I demonstrate this technique of bootstrapping on initial values in section 3.2.2.

3. Application to Test Cases

[19] I apply the mixing inversion method to both synthetic and real test data to demonstrate practical aspects of implementation. I first apply the method to synthetic data so that its performance can be evaluated for a well-defined problem, with particular emphasis on the impact of initial values on the parameter estimates. I then apply the method to a global compilation of oceanic $^{230}Th/^{232}Th$ versus

Table 1. Synthetic Test Inversion Results for Uniform Mixing Proportion Data (Figure 1a)[a]

	Depleted Component (#1)				Enriched Component (#2)				Concentration Ratio	
	X_1	σ_{X_1}[b]	Y_1	σ_{Y_1}[b]	X_2	σ_{X_2}[b]	Y_2	σ_{Y_2}[b]	c	σ_c[b]
True values	0.7036		0.513000		0.7370		0.512100		0.292	
Prior	0.7040	3.34e-04	0.512900	9.00e-06	0.7360	3.34e-04	0.512080	9.00e-06	0.4	0.1
Posterior	0.7044	2.30e-04	0.512900	2.15e-06	0.7362	4.30e-05	0.512100	4.23e-06	0.346	0.018

[a] Goodness-of-fit statistics: rms = 0.002, MSWD = 2.09; rms = normalized residual mean square (residual sum of squares divided by degrees of freedom) and MSWD = mean square of weighted deviates as defined by *McIntyre et al.* [1966].
[b] Standard error. Prior value defined by amplitude of Gaussian noise added to synthetic mixture data. Posterior value estimated with 1000 bootstrap replicates.

$^{87}Sr/^{86}Sr$ data (compilation from K. W. W. Sims and S. R. Hart (Comparison of Th, Sr, Nd, and Pb isotopes in oceanic basalts: Implications for mantle heterogeneity and magma genesis, submitted to *Earth and Planetary Science Letters*, 2005; hereinafter referred to as Sims and Hart, submitted manuscript, 2005)), and discuss some scaling issues along with the use of goodness-of-fit statistics to formulate hypothesis tests.

3.1. Synthetic Data

[20] I generate two sets of synthetic mixture data from hypothetical end-members as described in Appendix A. The first set of mixtures are formed by drawing mass fractions at random from the uniform interval [0, 1], and the second set of mixtures are formed by drawing random mass fractions from a Gaussian distribution centered on a mixing proportion of 0.5. Scatter about the mixing trend is introduced by adding Gaussian noise to both the x and y axis isotope ratios of each synthetic sample. For illustrative purposes I specify hypothetical depleted and enriched mantle sources in $^{143}Nd/^{144}Nd$ versus $^{87}Sr/^{86}Sr$ sample space. The end-members are meant to be suggestive of depleted and enriched components, but I purposefully avoid using published values to make clear I am not attempting to constrain the isotopic composition of mantle components. The synthetic mixture data are tabulated in the Appendix A.

[21] Initial guesses for the end-member ratios (including concentration ratio, or curvature) are required to start the inversion. From a practical standpoint, the guesses are used to start the iterative solver. Conceptually, the guesses represent the prior values, $\mathbf{z}_0$, that, along with prior covariance, cov $\mathbf{z}_0$, define the probability distribution (equation (10)) being maximized.

[22] I first apply the method to the synthetic data generated with a uniform distribution of mixing proportions. The inversion is started with initial guesses that are close to the true values, and it is able to "tune" the model to fit the data (Table 1, Figure 1a). In general, however, it may not be possible to choose initial end-member ratio values that are close to the true values. The critical issue is identifying the range of mixing proportions represented in the sample space. To illustrate the problem, I apply the method to the synthetic data set generated with a Gaussian distribution of mixing proportions. These data are clustered about a common mass fraction (Figure 1b). Initial values are chosen under the mistaken assumption that the samples span the entire range of mixing proportions, and the inversion is repeated (Table 2). As before, the inversion tunes the model to the data, but there are no gradients in the solution space to move the end-member isotope ratio estimates along the mixing hyperbola. This is a natural consequence of the fact that any set of end-members on the mixing hyperbola fit the data equally well. If it were somehow possible to know that the samples represent only a limited range of mass fractions, then the initial guesses could be chosen accordingly, and satisfactory results could be obtained (Table 3, Figure 1c).

[23] Prior knowledge regarding the range of mass fractions represented in a given data set is thus a crucial aspect for obtaining accurate end-member ratio value estimates. The inversion has the effect of moving initial ratio estimates to the "nearest" point on the mixing hyperbola, where length is measured in probability terms (see section 3.2), but the inversion cannot correct for erroneous starting assumptions regarding sample mixing proportions.

3.2. Real Data

[24] I apply the method to a global, oceanic $^{230}Th/^{232}Th$ versus $^{87}Sr/^{86}Sr$ data set (compilation from Sims and Hart (submitted manuscript, 2005))

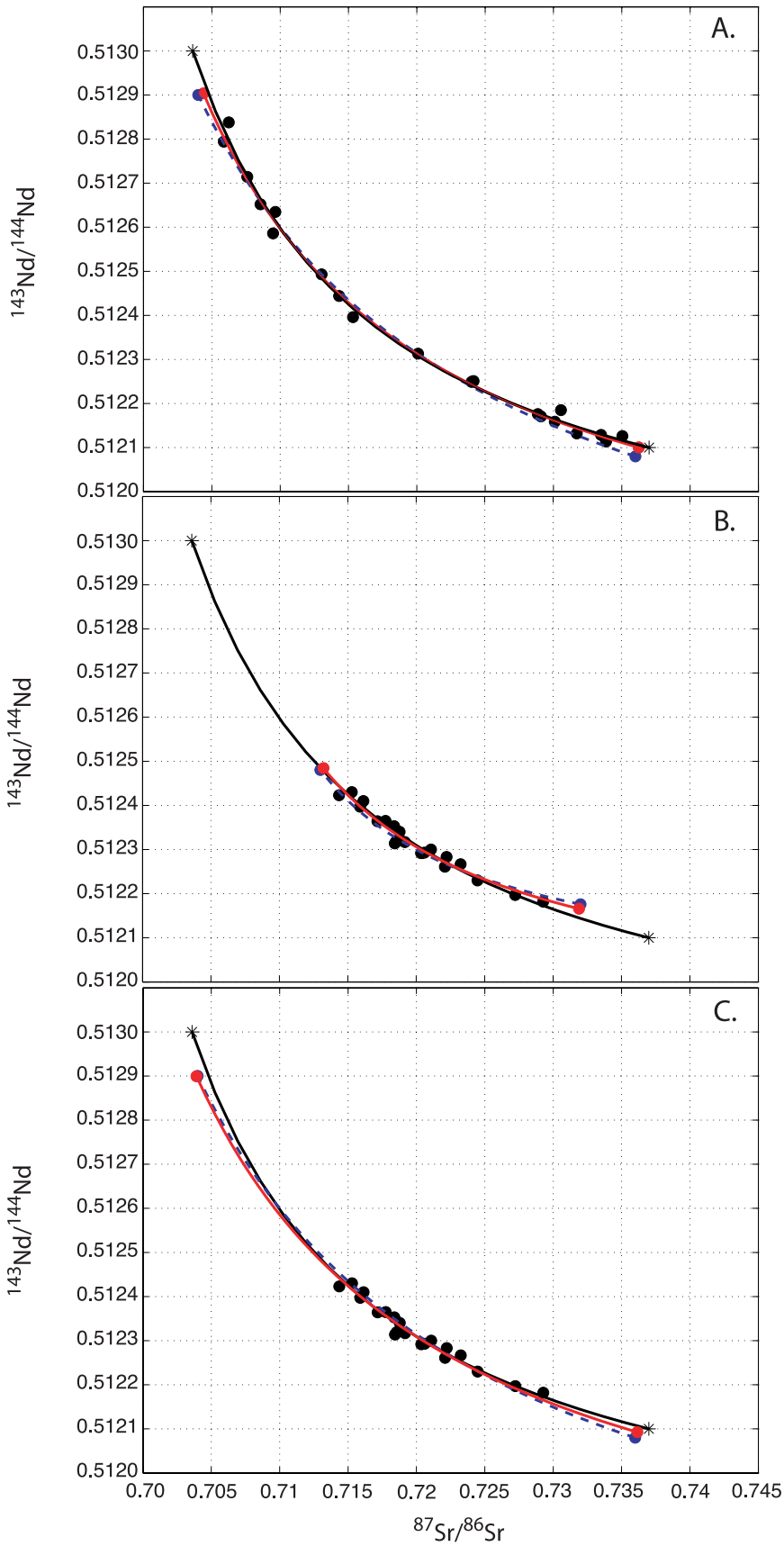
A.
B.
C.
$^{143}Nd/^{144}Nd$
$^{87}Sr/^{86}Sr$
0.5130
0.5129
0.5128
0.5127
0.5126
0.5125
0.5124
0.5123
0.5122
0.5121
0.5120
0.70
0.705
0.71
0.715
0.72
0.725
0.73
0.735
0.74
0.745

Figure 1

Table 2. Synthetic Test Inversion Results for Clustered (Gaussian) Mixing Proportion Data With Errant Initial Guesses for End-Member Ratio Values (Figure 1b)[a]

	Depleted Component (#1)				Enriched Component (#2)				Concentration Ratio	
	X_1	σ_{X_1}	Y_1	σ_{Y_1}	X_2	σ_{X_2}	Y_2	σ_{Y_2}	c	σ_c
True values	0.7036		0.513000		0.7370		0.512100		0.292	
Prior	0.7130	3.34e-04	0.512480	9.00e-06	0.7320	3.34e-04	0.512176	9.00e-06	0.4	0.1
Posterior	0.7132	1.50e-04	0.512484	2.55e-06	0.7319	3.85e-05	0.512166	3.54e-06	0.45	0.027

[a] Goodness-of-fit statistics: rms = 0.021, MSWD = 1.59.

for oceanic basalts (Figure 2) to demonstrate some considerations that arise in analysis of real data, including specification of the prior covariance matrix, estimation of parameter uncertainty, and the use of goodness-of-fit statistics for hypothesis testing.

3.2.1. Scaling of the Prior Covariance Matrix

[25] As described previously, the probability distribution being numerically optimized (equation (10)) is a function of the prior covariance matrix, cov $\mathbf{z}_0$. This matrix, which is effectively a weighting matrix for the model misfit penalty function, includes not only data measurement uncertainties, which are usually small, but also model parameter uncertainties, which may be poorly known and arbitrarily large.

[26] The mismatch between measurement error and model parameter uncertainty presents a scaling issue because large differences in the order-of-magnitude of the covariance matrix elements will degrade the numerical stability of the inversion. The elements of the covariance matrix (assumed diagonal) corresponding to the data uncertainties can be scaled by normalizing the data to zero mean and unit variance, and the element corresponding to the concentration ratio can be scaled by ordering the end-member components (i.e., X_1 versus X_2) such that any curvature is modeled with $c < 1$. But how should the prior covariance matrix elements corresponding to the end-member ratio uncertainties be scaled when the true uncertainties in real applications may be arbitrarily large? A simple solution that guarantees the numerical stability of the inversion is to set the prior end-member ratio uncertainties to the sample measurement uncertainties. Remembering that the prior covariance matrix is effectively a matrix of misfit penalty weights, this approach is equivalent to treating the initial values as additional data points when the misfit for a given iteration is calculated. In other words, the penalty for a mixing trend that does not pass through the initial values is the same as the penalty for missing an individual data point.

[27] For the $^{230}Th/^{232}Th$ versus $^{87}Sr/^{86}Sr$ global oceanic data compilation I make initial guesses assuming the samples represent nearly a complete range of mixture proportions, form a prior covariance matrix as described above, and generate parameter estimates (Figure 2, Table 4). I note that the gradient following solution moves the depleted (high $^{230}Th/^{232}Th$) end-member onto the mixing trend at a position that is inside the data field. This is allowed because the inversion is based on the general equation of the mixing hyperbola, which is not limited to the chord between the end-members. The initial values can be selected so as to force the parameter estimates outside the data field (e.g., Figure 1c), if necessary.

3.2.2. Model Parameter Uncertainty

[28] I estimate the standard error of the model parameters using both traditional bootstrapping and a Monte Carlo method for randomizing the

Figure 1. Synthetic test results. The true mixing trend through the synthetic samples (black dots) is shown by the solid black curve, with end-member component ratios shown as black stars at the endpoints. Initial guesses for the mixing model parameters are shown in blue, and the parameter estimates from the inversion are shown in red. The importance of prior knowledge regarding the range of mixing proportions represented in the sample set is shown via the progression of figures. The synthetic samples in Figure 1a have mixing proportions that are uniformly distributed over the entire possible range. The synthetic samples in Figure 1b are clustered about a mixing proportion of 0.5 (equal proportions of each end-member), but initial guesses are chosen under the errant assumption that the end-members lie just outside the data field. Synthetic samples in Figure 1c are identical to Figure 1b, but the initial guesses are the same as in Figure 1a. The inverse results and goodness-of-fit statistics are shown in Tables 1–3.

Table 3. Synthetic Test Inversion Results for Clustered (Gaussian) Mixing Proportion Data With Accurate Initial Guesses for End-Member Ratio Values (Figure 1c)[a]

	Depleted Component (#1)				Enriched Component (#2)				Concentration Ratio	
	X_1	σ_{X_1}	Y_1	σ_{Y_1}	X_2	σ_{X_2}	Y_2	σ_{Y_2}	c	σ_c
True values	0.7036		0.513000		0.7370		0.512100		0.292	
Prior	0.7040	3.34e-04	0.512900	9.00e-06	0.7360	3.34e-04	0.512080	9.00e-06	0.400	0.100
Posterior	0.7039	7.37e-05	0.512900	7.88e-07	0.7362	6.81e-05	0.512090	5.79e-06	0.365	0.012

[a] Goodness-of-fit statistics: rms = 0.023, MSWD = 1.76.

initial values (Table 4). The bootstrap estimates of standard error underpredict the uncertainty of the end-member ratios because they do not account for the influence of the initial values on the parameter estimates. The situation is improved when I use Monte Carlo methods to draw initial values at random from within specified intervals, and then use bootstrap methods to perform repeat inversions and generate estimates of standard error (Table 4). The concentration ratio error estimate is similar to the traditional bootstrap estimate, but, as expected, the end-member error estimates are much larger when the initial values are randomized.

[29] Standard error estimates formed by randomizing initial values have the desirable property that they respond to the hyperbolic curvature of the mixing trend. For example, the $^{87}Sr/^{86}Sr$ of the enriched component (X_2) is intrinsically more uncertain than that of the depleted component (X_1) because of the asymptotic nature of the mixing hyperbola. This effect is captured by the randomized initial value standard errors, but not by the traditional jackknife or bootstrap methods (compare values in Table 2). Randomizing initial values thus provides an effective means to incorporate realistic assessments of end-member uncertainty without compromising the scaling of the prior covariance matrix.

3.2.3. Goodness-of-Fit Statistics

[30] The quality of the model fit to the data can be assessed by forming goodness-of-fit statistics with the residuals. The residual mean square (rms) provides a quantitative measure of the "average"

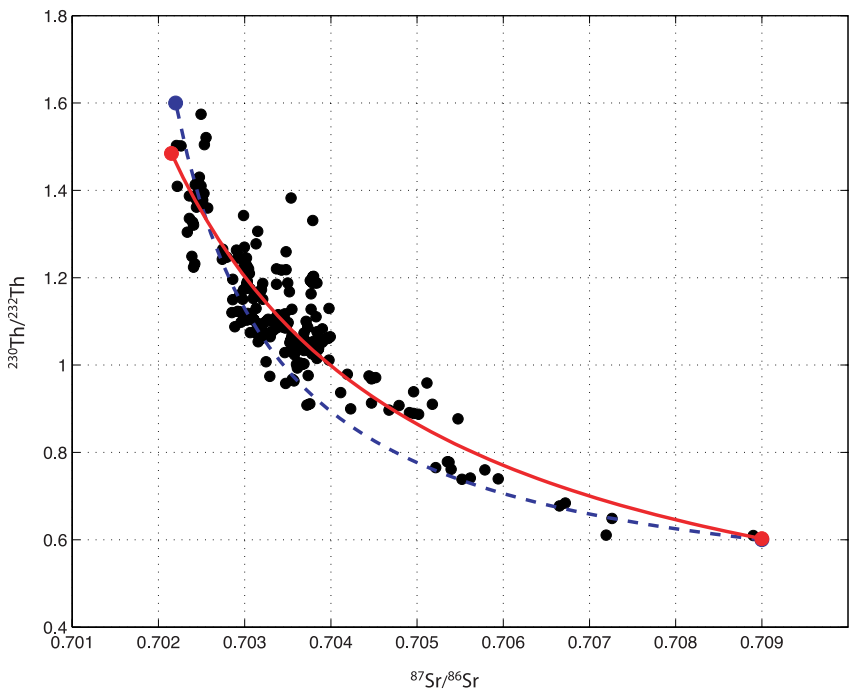

Figure 2. Inversion results for a global oceanic data compilation of $^{230}Th/^{232}Th$ versus $^{87}Sr/^{86}Sr$ (Sims and Hart, submitted manuscript, 2005). Initial model parameter guesses are shown in blue, and parameter estimates from the inversion are shown in red. The inverse results and goodness-of-fit statistics are shown in Table 04.

Table 4. Inversion Results for Global Oceanic $^{230}Th/^{232}Th$ Versus $^{87}Sr/^{86}Sr$ Compilation (Sims and Hart, submitted manuscript, 2005)[a]

	Depleted Component (#1)				Enriched Component (#2)				Concentration Ratio	
	X_1	σ_{X_1}	Y_1	σ_{Y_1}	X_2	σ_{X_2}	Y_2	σ_{Y_2}	c	σ_c
Prior	0.70220	1.00e-05	1.600	1.00e-02	0.7090	1.00e-05	0.600	1.00e-02	0.150	0.100
Posterior	0.70215	4.51e-06	1.485	2.11e-02	0.7090	8.75e-07	0.603	2.38e-02	0.301	0.034
		2.51e-06[b]		9.28e-02[b]		3.20e-04[b]		2.39e-02[b]		0.024[b]

[a] Goodness-of-fit statistics: rms = 0.182, MSWD = 60.66.
[b] Standard error estimate generated by perturbing initial guesses, as described in section 3.2.2.

squared residual, and when the data have been normalized to unit variance the RMS value represents the fraction of original variance about the mean that is not explained by the model. The RMS value of 0.182 for the $^{230}Th/^{232}Th$ versus $^{87}Sr/^{86}Sr$ data compilation (see Table 4) can therefore be interpreted to mean that 18.2% of the original data variance remains unexplained by the binary mixing model, or, conversely, that the model explains 71.8% of the original variance.

[31] The mean square of weighted deviates (MSWD) is another misfit statistic commonly employed in geochemical data analysis [e.g., *Brooks et al.*, 1972; *McIntyre et al.*, 1966]. The MSWD statistic quantifies the ratio of model misfit to measurement uncertainty along each coordinate axis. The MSWD value of 60.7 obtained for the $^{230}Th/^{232}Th$ versus $^{87}Sr/^{86}Sr$ data compilation demonstrates that the model misfit is significantly larger than the measurement error, indicating that processes other than binary mixing of two pure end-members are contributing variability to the sample isotope ratios. Possible sources of unmodeled variability are discussed by Sims and Hart (submitted manuscript, 2005) and include the contribution of additional components to the sample mixtures, as well as processes such as fractionation, in-growth, and weathering.

[32] Goodness-of-fit measures can be used to assess the statistical validity of binary mixing as a model for the variations observed in the $^{230}Th/^{232}Th$ versus $^{87}Sr/^{86}Sr$ data. The simplest test is against the null hypothesis that the observed variations are random. To do this, the F statistic is first quantified, which measures the variance reduction achieved by the model (72%) compared to the number of model parameters (5) and the degrees of freedom of the inverse problem ($N - 6 = 204$), yielding a value of 418 [e.g., *Weisberg*, 1985]. This quantity is then compared to a critical value by evaluating the F distribution for the appropriate degrees of freedom at a specified confidence level. To test against the null hypothesis at the 95% confidence level, for example, the critical value is $p = F^{-1}(0.95|5,204) = 2.26$. The F statistic for the model fit (418) is significantly greater than the critical value, providing strong evidence in support of binary mixing as a better statistical model for the data than random variation about the mean. More powerful statistical tests could be formulated by specifying stronger alternative hypotheses (e.g., in-growth and time effects, multicomponent mixing), but this is beyond the scope of this paper.

4. Conclusions

[33] I have derived a general method for fitting binary mixing models to ratio-ratio data. The method provides well-constrained estimates of the concentration ratio parameter, which controls the hyperbolic curvature of the mixing trend, and is able to move initial guesses for the end-member ratios onto the best-fit hyperbola. The positions of the end-members on the best-fit hyperbola, however, are underdetermined unless the mixing proportions of the samples are known a priori, which is not generally possible. The method should therefore be viewed as providing a means of tuning the initial end-member ratio guesses to the data.

[34] Nonparametric methods are best suited to estimating model parameter uncertainties, but uncertainty estimates for the end-member ratios must be treated with caution. Traditional implementations of the jackknife and bootstrap may severely underestimate the uncertainty of the end-member ratios because they fail to account for the influence of the initial guesses on the parameter estimates. Monte Carlo methods can be used to improve the situation by randomizing the initial guesses and generating repeat estimates. This can be thought of as a nonparametric implementation of Bayesian

methods where the distribution used to draw random values for the initial guesses is the prior, and the empirical distribution of repeat parameter estimates is the posterior. A more restrictive prior will result in a more restrictive posterior, and so forth, such that the size of the posterior uncertainties scale directly with the size of the prior uncertainties.

[35] Goodness-of-fit statistics can be used to assess the model fit to the data, and to form hypothesis tests to compare the fit of the binary mixing model against other models for the observed variations. The simplest test is against random variation, but the methods are general such that the variance reduction of any two models can be compared with their degrees of freedom via the F test to identify the best statistical fit.

[36] Matlab software to implement the inversion methods described in this paper can be downloaded as described in Appendix B.

Appendix A: Synthetic Test Data

[37] Synthetic data were generated by drawing random samples from a hypothetical $^{143}Nd/^{144}/Nd$ versus $^{87}Sr/^{86}Sr$ mixing trend. The hypothetical end-members have values of; (1) ''depleted'' $^{87}Sr/^{86}Sr = 0.703600$, $^{143}Nd/^{144}/Nd = 0.513000$, (2) ''enriched'' $^{87}Sr/^{86}Sr = 0.737000$, $^{143}Nd/^{144}/Nd = 0.512100$, and a concentration ratio of 0.292. The synthetic mixtures were generated by first drawing a mass fraction (mixing proportion) value at random from a specified distribution, calculating the mixture isotope ratios, and then adding random noise to simulate the variations observed in real data. Two different distributions were used to randomize the mass fractions: a Uniform distribution on the interval [0 1], and a Gaussian distribution with a mean value of 0.5 and a standard deviation of 0.12. The standard deviation of the Gaussian noise was set to 1/100 the total variation between the end-members for each ratio. The synthetic data values are provided in Tables A1 and A2.

Table A1. Synthetic Samples Generated From a Uniform Distribution of Mixing Proportions

Synthetic Sample	$^{87}Sr/^{86}Sr$	$^{143}Nd/^{144}Nd$
1	0.715320	0.512396
2	0.730543	0.512185
3	0.731711	0.512132
4	0.706240	0.512838
5	0.735044	0.512126
6	0.720084	0.512313
7	0.724002	0.512249
8	0.714307	0.512444
9	0.709652	0.512635
10	0.707595	0.512714
11	0.728858	0.512176
12	0.724149	0.512251
13	0.733841	0.512114
14	0.729080	0.512171
15	0.709474	0.512586
16	0.730106	0.512159
17	0.713025	0.512493
18	0.733479	0.512129
19	0.705876	0.512794
20	0.708566	0.512652

Table A2. Synthetic Samples Generated From a Gaussian Distribution of Mixing Proportions

Synthetic Sample	$^{87}Sr/^{86}Sr$	$^{143}Nd/^{144}Nd$
1	0.717760	0.512365
2	0.718389	0.512353
3	0.715292	0.512430
4	0.719178	0.512317
5	0.727236	0.512197
6	0.718439	0.512314
7	0.723245	0.512267
8	0.720360	0.512292
9	0.721081	0.512300
10	0.729280	0.512182
11	0.718778	0.512340
12	0.714367	0.512423
13	0.717161	0.512364
14	0.724478	0.512230
15	0.716137	0.512410
16	0.715896	0.512397
17	0.722222	0.512283
18	0.718556	0.512319
19	0.720605	0.512293
20	0.722096	0.512261

Appendix B: Software

[38] *Matlab* scripts to perform the mixing inversion described in this paper can be downloaded from ftp://obslab.whoi.edu/pub/ras/Software. Digital files with the synthetic test data sets are also available to benchmark results.

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References

Albarede, F. (1995), *Introduction to Geochemical Modeling*, 543 pp., Cambridge Univ. Press, New York.

Brooks, C., et al. (1972), Realistic use of two-error regression treatments as applied to rubidium-strontium data, *Rev. Geophys.*, *10*, 551–577.

Efron, B. (1987), Better bootstrap confidence intervals, *JASA J. Am. Stat. Assoc.*, *82*, 171–200.

Langmuir, C. H., et al. (1978), A general mixing equation with applications to Icelandic basalts, *Earth Planet. Sci. Lett.*, *37*, 380–392.

McIntyre, G. A., et al. (1966), The statistical assessment of Rb-Sr isochrons, *J. Geophys. Res.*, *71*, 5459–5468.

Menke, W. (1989), *Geophysical Data Analysis: Discrete Inverse Theory*, 2nd ed., 289 pp., Elsevier, New York.

Sohn, R. A., and W. Menke (2002), Application of maximum likelihood and bootstrap methods to nonlinear curve-fit problems in geochemistry, *Geochem. Geophys. Geosyst.*, *3*(7), 1041, doi:10.1029/2001GC000253.

Tarantola, A., and B. Valette (1982), Generalized non-linear inverse problems solved using the least squares criterion, *Rev. Geophys.*, *20*, 219–232.

Vollmer, R. (1976), Rb-Sr and U-Th-Pb systematics of alkaline rocks: The alkaline rocks of Italy, *Geochim. Cosmochim. Acta*, *40*, 283–295.

Weisberg, S. (1985), *Applied Linear Regression*, 2nd ed., 324 pp., John Wiley, Hoboken, N. J.