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Key Points:

- Nonisochronous data are treated as a discrete mixture of isochrons
- Re-Os bitumen data may preserve source and emplacement information
- A new tool to distinguish disturbed and undisturbed samples

Supporting Information:

- Supporting Information S1
- Data Set S1
- Figure S1
- Figure S2

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Investigating Complex Isochron Data Using Mixture Models

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Abstract The isochron technique for dating geological events is widely used in many fields of isotope geochemistry. However, data sets can be complex, and many samples may not behave as closed systems, resulting in excess scatter around a regression line. In certain data sets, however, excess scatter may result when geological samples are partially reset or when samples are comprised of multiple components recording different geological processes separated in time and/or initial isotope composition. Here we introduce a new approach for investigating evidence of such multicomponent mixtures within isochron space. We provide a mathematical framework to resolve the number of mixture components, without requiring any prior knowledge of this number. Crucially, the model reports the proportion of each individual sample that belongs to each mixture component, allowing the user to return to the samples and independently test model outputs with other techniques. It is important to distinguish accurate and meaningful ages and initial daughter isotope compositions from the meaningless values that are caused by mismatch between geological processes and the models that we use to describe them. First, we demonstrate our new model on a synthetic data set to show that it can successfully separate distinct isochrons in a complex mixture. We further validate our approach with a previously published data set using the ¹⁸⁷Re–¹⁸⁷Os system in bitumen and ¹⁴⁷Sm/¹⁴⁴Nd system in magmatic rocks. We identify discrete components in these data sets and using complementary geological observations discuss the implications of treating these scattered data as recording multiple geological processes.

1. Introduction

Isochrons, which were introduced by Nicolaysen (1961), are specific situations where a positive correlation exists between the abundance of a radiogenic daughter isotope and its radioactive parent isotope with both normalized to a stable, nonradiogenic isotope of the daughter element. This correlation is the result of radiogenic ingrowth of the radiogenic daughter. For instance in the Re–Os isotope system ¹⁸⁷Os/¹⁸⁸Os is plotted against ¹⁸⁷Re/¹⁸⁸Os, and the system can be referred to as an isochron if the correlation of the data has geochronological significance. In the classical approach, isotope data are treated using a least squares regression where the slope of the line is proportional to the age of the system and the y-intercept gives the initial isotope ratio (hereafter *initial*) of the system at the time of formation or equilibration (McIntyre et al., 1966; York, 1966; York et al., 2004). For the calculated age and initial to be geologically meaningful, three critical assumptions need to be met: (1) All of the samples have the same initial isotopic composition at formation age; (2) all of the samples are the same age; and (3) the system has remained close since formation (e.g., no parent or daughter isotope loss or gain). If these assumptions are met, the isochron technique can provide a robust and precise method for dating geological samples and has been widely applied to many isotope systems (e.g., Sm–Nd, Rb–Sr, Lu–Hf, and Re–Os) from many types of geological materials.

Since its introduction in the 1960s the isochron technique is still the only method for dating many samples, and it has therefore remained highly popular to the present day. Variations in data reduction have been suggested to improve the robustness of the interpretations of the isotope composition data. These include (1) improving the least squares regression technique to deal with non-Gaussian behavior at the edges of the distribution (e.g., Powell et al., 2002); (2) introducing statistical tests, such as the mean square weighted deviation (MSWD), to determine how well the data and associated uncertainties are described by a given regression (Brooks et al., 1972, 1968; McIntyre et al., 1966; York, 1968); and (3) accounting for correlations between the ratios (e.g., McLean, 2014; York, 1968). Also, the introduction of models 1, 2, and 3 isochrons

Figure 1. Schematic diagram showing how multistage evolution can disrupt and create separate isochrons over time. (a) A perfect isochron. (b) A resetting event has occurred; however, the isochron is not perfectly reset. Orange points mark those that have been perfectly reset, the gray points reflect those that have been partially reset, and the blue points represent samples that have not been reset. (c) As time progresses after the partial resetting event, the samples all rotate and become closer together, producing an array with a meaningless age, initial, and a high mean square weighted deviation (MSWD; shown by the thick black line).

in isoplot (Ludwig, 1991, 2003) was highly influential not just for isochrons but geochronology in general, providing a simple Excel-based tool for robust statistical analysis. Model 1 isochrons treat scatter around the regression line in terms of analytical error only (following the equations of York, 1968), model 2 isochrons assign an error correlation coefficient of zero to all data points and weight each point equally in the regression, and model 3 isochrons consider scatter around a regression line as due to a combination of the assigned errors plus a normally distributed unknown component in the Y axis values (similar to the algorithm of McIntyre et al., 1966).

The realization that samples with correlated variations in initial daughter isotopic compositions and parent/daughter ratios can create pseudoisochrons with meaningless age information (Chauvel et al., 1985; Davidson et al., 2005; Juteau et al., 1984; Zheng, 1989) suggests that the isochron dating method may not always retain robust age or isotopic information. Furthermore, in many geological settings, the assumptions that validate the isochron method cannot be met; for example, metamorphic terranes often have disturbed Rb-Sr and Sm-Nd systems because of multiple metamorphic and fluid alteration events (e.g., Bikerman et al., 1975; Gruau et al., 1990), while oils typically have highly scattered Re-Os systematics (Cumming et al., 2014; Finlay et al., 2011, 2010; Lillis & Selby, 2013). In many situations the processes leading to scattered data can be viewed as discrete. For example, if multiple sources are isotopically heterogeneous (e.g., mixing of different oils), then a data set may consist of samples that started with different initials. Or if multiple sources have different ages (e.g., detrital mixtures of different tephra layers), a complex combination of discrete components can be formed. Also, in scenarios where a subset of a sample is isotopically disturbed (e.g., by a secondary metasomatic event), this creates disturbed isotope systematics containing discrete components.

Disturbed radiogenic systems producing scattered data may also occur in some specific cases due to partial resetting of the radiogenic daughter isotope composition (Figure 1). In our synthetic example, we make an assumption that the system has the ability to completely rehomogenize during the resetting. This means that samples with radiogenic (or unradiogenic) daughter isotope compositions can change such that they reflect the average composition of the whole suite of samples. In reality this is an oversimplification because samples will first equilibrate with the material surrounding them, creating local equilibrium rather than system wide equilibrium. The ability to completely reset the daughter isotope composition is related to the time and temperature history of the samples as well as other factors that control diffusion of that particular element throughout the whole sample suite. Despite these caveats, we use the example in Figure 1 to indicate how multiple mixtures may arise in data sets that have been disturbed.

Partial resetting of a suite of samples results in a data set that represents a complex mixture of components consisting of completely reset, partially reset components and possibly also components that have not been

affected by the resetting (Figure 1b). As time progresses, radiogenic ingrowth of the daughter isotope continues, and, due to the structure of the isochron diagram, all of the aliquots appear to roughly converge (Figure 1c; Davidson et al., 2005; Juteau et al., 1984; Zheng, 1989). Using the classical isochron approach, these aliquots would form an isochron that results in a meaningless *average* age and initial with a high MSWD. Over geological timescales, however, the processes that initiate radiogenic ingrowth, or the processes that reset radiogenic systems, can be viewed as discrete events. Thus, if a sample is only partially reset, multiple discrete components can be identified (Figure 1c), which contain isochrons with possibly meaningful ages and initials (i.e., the event resetting the radiogenic system) and isochrons with potentially meaningless ages and initials (i.e., partially reset samples). It should be noted however that if all samples are perfectly reset, or if all samples are partially reset, this would result in a data set consisting of a single discrete component and alternative methods would be required to extract the *end members* of a single continuous mixture.

To investigate for evidence of complex discrete mixtures in isochron data, we utilize a mixture model to extract the possible ages and initials of independent isochrons within a data set. We then report which data points, or proportions of each data point, belong to each modeled isochron. This provides the ability, using other analytical or geochemical tools, to independently verify the grouping of data points that the model suggests and identify which ages and initials are meaningful. We demonstrate the ability of the model to resolve mixtures and discuss the different types of mixtures that may be present in geologic data sets. We then test the utility of our method with two previously published data sets, one whole-rock Sm-Nd data set from the Vetreny lavas in Fenoscandia (Puchtel et al., 1997, 2016) and another using bitumen Re-Os data set from the Polaris MVT (Mississippi Valley Type) deposit in Canada (Selby et al., 2005). Our approach allows us to statistically deal with excess scatter while providing geologically reasonable, and indeed more informative, results. It is important to note, however, that our model identifies potential clusters within a data set and these need to be independently verified by further geochemical techniques to determine if they have geological and/or geochronological meaning.

2. Mixtures in Geological Systems

Individual isochrons can be interpreted as a single discrete event, but in reality they represent geological processes that are, to some degree, continuous. For example, continuous mixtures are often interpreted in fission track (Galbraith & Laslett, 1993) and U-Th-He thermochronology (Vermeesch, 2010) where the true age distribution in a sample is assumed to follow a log-normal distribution and could represent, for example, mineral growth over a period of time. These processes produce dispersion that can be effectively described by using an MSWD and least squares regression. Modeling and interpretation of continuous geological processes depend crucially on the temporal sensitivity of the radioactive decay system and the resolution of the analytical technique used. The complexities associated with continuous processes can also be compounded when multiple geological events have influenced the isotopic composition of a given sample set, resulting in multiple isochrons that may or may not be independently resolved from one another. Each individual event may have introduced further dispersion to the total data set.

To help visualize the processes that create continuous and discrete mixtures, we use two synthetic Rb-Sr isochrons as examples, one representing an idealized isochron from an erupted lava that cooled rapidly and the other representing an idealized isochron from an intrusion that cooled slowly and therefore represented a continuous mixture. Figure 2a represents the eruptive example and is a single discrete event, showing a perfect 2-Ma isochron (model 1 from Ludwig, 1991, 2003) with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7. Figure 2b shows the kernel density distribution of all possible ages and initials from isochrons calculated using pairs of data points from the data set (including the analytical uncertainty; see below for more detail). The isochron and the tight kernel density distribution given by all possible isochrons can be thought of as fast cooling of an erupted magma that had a homogeneous Sr isotopic composition and a range in Rb/Sr ratio. In this example the system can be thought of as a single discrete mixture event since the dispersion seen in the kernel density distribution (Figure 2b) and the error on the age and initial are due to analytical errors.

A slowly cooling intrusion can be thought of as a continuous mixture using some concepts from thermochronology. To illustrate this, we created a similar isochron to the discrete example but added much more random scatter to the initial $^{87}\text{Sr}/^{86}\text{Sr}$ before computing the Sr isotope evolution over 2 Ma. This created an isochron (model 3 from Ludwig, 1991, 2003) with a high MSWD and a slightly older age (Figure 2c). The kernel density

Figure 2. Schematic diagram showing the difference between discrete and continuous mixtures using an Rb-Sr isochron as an example. (a) A perfect model 1 (Ludwig, 1991, 2003) isochron representing a discrete mixture. (b) A kernel density estimate of the ages and initials from the data in Figure 2a. (c) A model 3 isochron (Ludwig, 1991, 2003) representing a continuous mixture. (d) A kernel density estimate of the ages and initials from the data in Figure 2c. MSWD = mean square weighted deviation.

estimate of all possible ages and initials is much more dispersed than the discrete example (Figure 2d). Extra dispersion can be easily explained by considering a variety of minerals with different closure temperatures to Sr diffusion in the intrusion as it cools. The older age is a random artifact of this example and is not intended to be geologically significant.

An isochron though the Rb-Sr data in Figure 2c essentially represents an average age and initial Sr isotope composition for the samples since the system as a whole is a continuous mixture between the times and temperatures when Sr diffusion begins to close and when it completely closes, through the time of magmatic cooling. The same concepts can be applied to grain size variations since larger grains have higher closure temperatures to diffusion than smaller grains. In a continuous mixture, the important ages are at the edges of the distribution since they represent the timing of an actual event, that is, the time that the system fully closes and the time that the system starts to close. Also important to consider are the analytical uncertainties, which create extra dispersion; however, an isochron age itself in a continuous mixture is a *meaningless* average and may not have geological significance (assuming that the analytical uncertainties are small enough to be able to resolve the real age and initial dispersion).

The approach presented here is a discrete mixture model and should not be used to identify the end members of continuous mixtures or the onset and cessation of continuous geological processes. To show the ability of the model to distinguish discrete mixtures, we developed a synthetic data set containing multiple discrete isochrons that are randomly mixed. We then highlight the utility of the model using previously published natural data where mixing of different components could explain the dispersion in the observations.

3. Methods

In assuming that multiple isochrons may exist within a given data set, we add an additional assumption to the single isochron approach. From a statistical perspective this equates to the assumption that the data can be described by multiple linear regressions. This is accomplished in what is generally known as a finite mixture model. More specifically, we use latent class regression, where each latent class reflects a subgroup of observations, in this case, a possible isochron. The finite mixture distribution is given by the following equation:

$$h(y|x, \psi) = \sum_{k=1}^K \pi_k f(y|x, \theta_k),$$

where h is the conditional density, y the dependent variable (radiogenic daughter/stable daughter), x the independent variable (parent isotope/stable daughter), and ψ the vector of all model parameters. Each latent class represents a component (k) that is described by a linear regression (θ_k) with slope β' and prior probability (π_k ; i.e. individual isochron). The errors on each regression are assumed to fit a normal distribution with standard deviation σ .

$$\theta_k = N(\beta'_k, \sigma_k)$$

To simplify the nomenclature of the model, we use the terms *component* and *cluster*, with components referring to the number of isochrons the model attempts to fit to the data and cluster referring to the data belonging to a specific isochron.

To implement this approach, a script has been written, which utilizes the *Flexmix* package in the R statistical computing environment (Leisch, 2004). Models are fitted using an iterative expectation-maximization (EM) algorithm, in which the posterior probabilities of each datum belonging to each cluster are estimated, and the component-specific log-likelihood is maximized to attempt to ensure that the best fitting model is found. The model is run for a range of components (possible isochrons) and is initialized randomly so that data are assigned to a cluster based on the posterior probability distribution in a pseudo-Bayesian approach. For each component the EM algorithm is repeated to reduce the possible impact of poor initialization values. For each repetition, the EM algorithm is run until either the iterative improvement in log likelihood falls below a pre-specified threshold or the maximum number of iterations is reached (we typically use ~300 repetitions to ensure a reasonable model fit without being overly computationally expensive). The model outputs a table after it has finished, which indicates if the EM algorithm has converged or not; of course, the results should only be trusted if the model converges. The number of repetitions and iterations can both be specified; it is usually preferable to use a higher number for the iterations than the repetitions (typical values may be 50 repetitions and 300 iterations). Finally, a threshold can be set for the prior probability of a cluster, so that any clusters that fall below this value are removed in the iterative process, which greatly reduces the possibility of model overfitting; a common number to use for this prior is the number of data in the data set divided by 2, since this will ensure that all suggested components involve two or more data points. Consequently, the total number of clusters suggested by the model in a data set may be lower than the specified number of components.

To account for the analytical error in isotope measurements, a synthetic data set for each data point is created prior to running the *Flexmix* model. The synthetic data set is a normally distributed point cloud that represents the uncertainty in each respective input data point. The finite mixture model is then run using the synthetic data set from all input data points combined. However, it requires an additional assumption to be made, depending on whether an individual analysis (and its corresponding synthetic data set) can belong to multiple clusters or can only belong to a single cluster (or isochron). This will depend upon the geological assumptions that are made. In the case where an individual analysis can only belong to a single cluster, this is modeled using random effects, where all points from the synthetic data set of an individual datum must belong to the same cluster. In the case when an individual analysis may belong to multiple clusters, the model quantifies the proportion of each point cloud that belongs to each cluster; all of the following examples allow individual analyses to belong to multiple clusters.

Once the model is run, the best fitting results for each of the components in the chosen range are extracted. The ability of these respective models to fit the data is compared using the integrated classification likelihood

(ICL) criterion (Biernacki et al., 2000). The ICL is an adaptation of a more commonly employed model comparator, the Bayesian information criterion (BIC). The BIC is a penalized likelihood function, meaning that it is a measure of the efficiency of the posterior distribution to fit the data (i.e., how likely the mixture of isochrons fits the data) penalized by the number of parameters in the model, which is increasing with the number of mixture components the model identifies. Commonly, the penalization term is positive, and the likelihood is negative, meaning that the lower the value of the BIC, the better fitting a model is. The ICL differs in that it includes an extra penalization term that corresponds to the estimated mean entropy. Thus, the ICL will prefer clustering the data into nonoverlapping groups, meaning that it will better identify the number of clusters in the data in comparison to the BIC (Baudry et al., 2010; Bertolotti et al., 2015; Hamdan & Wu, 2013). Consequently, with increasing number of mixture components the optimum value of the ICL commonly appears as a trough (see figures in the supporting information), after which the penalization terms (model complexity and entropy) outweigh any marginal increase in the efficiency of the posterior model fitting the data.

For users that would prefer to use the Akaike information criterion or BIC model comparators, the model outputs a table after it has finished running, which indicates if the EM algorithm has converged (which must be the case if the results are to be trusted), and it also provides the ICL, Akaike information criterion, and BIC model comparator values for all numbers of components.

The results of the model are presented in two ways. First, the ages and initial isotope compositions of the modeled isochrons are plotted as red diamonds and are automatically labeled with their cluster as assigned by the model. Second, a 2-D kernel density estimate of all possible isochrons present within the data set is plotted behind the modeled isochrons (called the background plot). This background plot is created by calculating the age and initial of all two-point isochrons; this is created by connecting all points from the synthetic data set (the data set that accounts for analytical uncertainties). Unreasonable ages (negative ages and negative initials) are filtered out.

The 2-D kernel density estimate of all possible isochrons is colored so that dominant ages and initials within the data set show up as dark gray to black and fade to white as the proportion of data producing given ages and initials reduces. The background plot is designed as an independent internal check on the isochrons identified by the Flexmix analysis, since isochrons that reflect large portions of the data should align with the dark areas in the background plot. Isochrons defined by the model that do not align with areas identified by the background plot should be treated with caution and may represent artifacts. Additionally, the shape of dark areas in the background plot can provide general information about the uncertainties associated with any modeled isochrons (see below for examples). The model does not provide the uncertainties in age and initial isotope composition for the modeled isochrons since individual data points are partitioned between isochrons creating artificiality low uncertainties. Isochrons with few data points or corresponding to highly scattered data show up as diffuse lightly colored areas in the background plot, and the modeled isochron (shown as a red diamond) may not plot exactly in the center of the shaded area. Modeled isochrons belonging to well-resolved linear arrays in the data without much scatter will correspond with dark circular spots in the background plot; see below for examples (and also the supporting information). Finally, the model has been programmed to work with most commonly used isochron-based geochronologic systems (Rb-Sr, Sm-Nd, Lu-Hf, and Re-Os) but would be possible with any decay system (e.g., U-Pb and Hf-W).

4. Test Case: Mixing Between Multiple Isochrons

To investigate the ability of the model to distinguish multiple components, a synthetic data set that mimics a random mixture of two Rb-Sr isochrons has been created. We use a 2,000-Ma isochron that has an initial isotopic composition of 0.7 and a second isochron with a 0 age and an initial of 0.86. We then produce a data set containing 200 data points with 40% of the points lying on either of the two isochrons and 60% of the data representing a random mixture between the two (Figure 3a). For simplicity, we do not model any scatter within each end-member isochron. While this may be geologically unrealistic, this scenario highlights the ability of the model to correctly identify discrete components and distinguish isochrons that may contain meaningful age and initial information from isochrons that may contain meaningless age and initial information of a continuous mixture. Importantly, adding a component of scatter to data in this example does not significantly alter the results. The values for the ICL parameter show a steep decline between two and

Figure 3. Model results from a discrete mixture data test. (a) The input data are shown in red consisting of two isochrons, the first with an age of 2,000 Ma and an initial of 0.7 and the second with an age of 0 Ma and an initial of 0.86; the other data points reflect a random mixture between the two isochrons. (b) The model output for three components with the background plot showing the distribution of all possible isochrons in the data set.

three components, clearly preferring three rather than two (shown in the supporting information). The second panel, Figure 3b, shows the model results for three components (results for all components from two to nine are shown in the supporting information). The three-component result contains two clusters that exactly match the two isochrons and a third cluster that lies directly between the two (Figure 3b). This intermediary cluster (cluster 2 in this case) effectively removes the continuously mixed data, resulting from mixing between two end members. The background plot is dark at the locations of the two isochrons representing specific events, grades toward lighter colors representing the data that falls in-between, and is very light at the location of the intermediary cluster 2. The presence of such intermediary clusters must be interpreted cautiously, as they may not represent geologically meaningful ages or initial isotope compositions. In fact, all clusters identified by the model should be treated cautiously, and other geological information should be used to determine if they reflect real events/processes or not. In the case where all 100% of the data are randomly mixed between the two end-members, the model identifies one discrete component as the best fitting model. This would have a high MSWD and provide meaningless information.

5. Geologic Examples

5.1. Re-Os Analysis of Bitumen From the Polaris MVT Deposit

Re-Os analyses of oils or other petroleum derivatives often exhibit a high degree of scatter in isochron space that is often not convincingly explained (e.g., Cumming et al., 2014; Finlay et al., 2011; Lillis & Selby, 2013). The Re-Os technique is the only method currently able to isotopically date such samples, and thus, any method that extracts more reliable information from these data is a powerful tool that can be used to complement basin-deposition, oil-production, and petroleum system models. Here we show that excess scatter in bitumen Re-Os data can be explained by assuming that the data represent a mixture of isochrons. We illustrate this point using a data set from the Polaris MVT deposit in Canada (Selby et al., 2005).

The Polaris MVT deposit is one of the world's largest Pb-Zn deposits, with an original ore reserve of ~22 Mt. The metals are hosted by Upper Ordovician carbonates of the Thumb Mountain formation on Little Cornwallis Island in the Arctic Archipelago, Nunavut, Canada. Thumb Mountain carbonates are part of a carbonate-chert-evaporite-shale-sand Cambrian-to-Devonian shelf sequence that lies on Neoproterozoic basement (Kerr, 1977; Okulitch & Packard, 1986). The dominant ore minerals (galena and sphalerite) were emplaced as veins or open space fills; the fluid transporting the ore also created extensive dolomitization of the limestone (Randell & Anderson, 1990) and presumably originated from either Precambrian basement or younger sediments above (Savard et al., 2000). The bitumen in the deposit appears to have formed just after the main ore-forming event since the bitumen is space filling and occurs as late coatings on ore minerals. While the ultimate origin of the bitumen remains unclear, the Pb-Zn mineralization has been dated to 366 ± 15 Ma using Rb-Sr in sphalerite (Symons & Sangster, 1992). The Re-Os isochron age for all of the

Figure 4. Model output figure panel showing the results from the Selby et al. (2005) data. (a) Modeled isochrons plotted through the clusters suggested by the model; each isochron is colored differently. The synthetic data sets representing each data point from the Selby et al. (2005) data set are also shown. (b) The model results panel with the clusters and background figure for the modeled isochrones shown, along with the isochrons from Selby et al. (2005) indicated as stars, the estimated $^{187}\text{Os}/^{188}\text{Os}$ of Ordovician seawater is shown as a blue bar, the Rb-Sr sphalerite age of 366 ± 15 is shown, and the age of the sediments hosting the deposit is shown as a yellow bar (note that the age of the sediments also increases outside of the range of the figure).

bitumen samples gives a much older age of 411 ± 18 Ma and an $^{187}\text{Os}/^{188}\text{Os}$ initial of 0.82 ± 0.28 (Selby et al., 2005). However, an MSWD of 186 (Selby et al., 2005) indicates that the assumptions for an isochron have not been met. To improve the isochron, Selby et al. (2005) used the Rb-Sr sphalerite age and the measured $^{187}\text{Re}/^{188}\text{Os}$ to calculate the $^{187}\text{Os}/^{188}\text{Os}_i$ of each analysis at 366 Ma. They then plotted all samples with similar initials on a new isochron, which yields an age of 374.2 ± 8.6 Ma with an MSWD of 11.7. However, filtering the data this way is circular (i.e., using a predetermined age to identify samples with the same initial at a preselected age, then regressing those samples to determine an isochron age) and would not be possible without prior knowledge of the data set's assumed age. Our modeling approach provides an alternative method for data interpretation not based on prior assumptions, which highlights the validity of our method.

To model the Selby et al. (2005) data, we used a synthetic data set of 100 points to represent each Re-Os analysis, 100 repetitions of the EM algorithm for a range of components between one and seven, and we allowed the individual analyses to belong to different isochrons. The results of the model are displayed in Figure 4 and show that this bitumen Re-Os data set could be considered in the context of discrete mixtures. The modeled isochron ages range from the Rb-Sr sphalerite age (369 Ma) to 453 Ma (Figure 4). Interestingly, the youngest age (identical to the sphalerite age) accounts for only ~12.3% of the data whereas the oldest age accounts for ~35% of the data. The age clusters decrease in initial with increasing age from an $^{187}\text{Os}/^{188}\text{Os}$ ratio of ~1.5 at 369 Ma to ~0.1 at 453 Ma, potentially indicative of two end members with complex mixing between them (compare with Figures 1 and 4). The modeled isochrons also contain an age near the 411-Ma age suggested by the total isochron from (Selby et al., 2005). This age may represent an average between the oldest and youngest components, lending credence to the idea that this age may be a mixing age with little relevance for the timing of geological events.

The oldest age produced by the model (453 Ma) is identical to the Upper Ordovician age of the sediments that host the Polaris deposit; however, the low initial of ~0.1 for this age is lower the expected osmium isotopic composition of seawater at that time (~0.5–0.3; Turgeon et al., 2007; Widom et al., 2004; Figure 4b). Since organic shales can have orders of magnitude more Re and Os than oils (e.g., Finlay et al., 2012), we tentatively suggest that the old age may result from fine organic sediment powder from the Ordovician sediments being trapped within the bitumen, mixing with the isotopic data from the oils. The younger age determined by the model, 369 Ma, is identical to the Rb-Sr sphalerite age of the Polaris deposit itself (Figure 4b) and is obtained without filtering the data, indicating that bitumen most likely does, at least in part, record the age of emplacement. However, the low proportion of data (12.3%) that fall on this line suggests that relatively few of the data points record this age.

Table 1*Table Showing How the Model Partitions the Data of Selby et al. (2005) Between Different Clusters*

Re-Os sample from Selby et al., 2005	Probability that each data point belongs to a cluster				
	Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5
1 ^a	0	0	1	0	0
2	1	0	0	0	0
3 ^a	1	0	0	0	0
4 ^a	0.67	0	0.16	0.01	0.16
5	0.79	0	0.21	0	0
6	1	0	0	0	0
7	1	0	0	0	0
8 ^a	0	0.99	0.01	0	0
9 ^a	0	1	0	0	0
10	0	0.68	0	0.32	0
11 ^a	0	0	1	0	0
12	0.17	0.83	0	0	0
13 ^a	0	1	0	0	0
14 ^a	0.1	0	0.15	0	0.75
15 ^a	0	0	0	0	1
16 ^a	0.02	0	0.07	0.64	0.27
17 ^a	0.65	0	0.01	0.07	0.27
18 ^a	0.51	0	0.22	0.05	0.22
19 ^a	0	0	0	0	1
20 ^a	1	0	0	0	0
21 ^a	0.22	0	0	0.05	0.73
22 ^a	0	0	0	0	1
23	0	0	0	1	0
Percentage of data	35.3	19.6	12.3	9.3	23.5
Cluster age (Ma)	451.9	407.3	369.2	431.3	403.8

Note. Also highlighted are the samples used by Selby et al. (2005) to create the ~366-Ma isochron; note that some of the samples selected by Selby et al. (2005) are not considered to belong to the young cluster.

^aAnalysis selected by Selby et al. (2005) to represent the 366-Ma age.

The results from the mixture model can be compared to the subset of samples chosen by Selby et al. (2005) to reflect the age of the mineralization. The samples selected by Selby et al. (2005) are compared with the model selection in Table 1. All of the samples selected by the model to make the young isochron are also among those selected by Selby et al. (2005). However, seven other samples used by Selby et al. (2005) do not belong to that isochron, which is possibly an explanation for the high MSWD of 11.7 reported for the young age.

Further inferences about the Polaris deposit could be made if it is tentatively assumed that the oldest and youngest ages have geological significance and the intermediate ages are the result of mixing between these two end members. First, using the youngest age cluster, the Re-Os system in bitumen may be used to reliably date bitumen formation. The second inference requires an assumption that the bitumen originated from local, organic-rich rocks around the deposit, which are dated by the older Ordovician ages from the model. In this case, the Re-Os system in bitumen may not have been entirely reset by the oil formation and preserves some source age information. Rather than being seen as a weakness in the Re-Os technique, this preservation should be viewed as a strength, as these data provide both the age of the oil generation and information about the source of the oil, both pieces of information that are key to understanding petroleum systems. This suggestion is, of course, not proof that oils may retain source age information; however, it does indicate that further work should be conducted to determine if source information is actually preserved in bitumen samples.

5.2. Vetreny Belt Lavas and the Sm-Nd System

The Vetreny lavas are found in a 250-km long belt to the southeast of the Fennoscandian shield and are part of an exceptionally well-preserved supercrustal unit emplaced between ~2.41 and 2.44 Ga. The mafic and ultramafic lavas of the Vetreny belt, combined with mafic dyke swarms, flood basalts, and layered gabbro

Figure 5. (a) Model output figure panel showing the results from the Puchtel et al. (1997) Vetreny komatiite Sm-Nd data; the insert in the upper right shows the isochron diagram for the same data with the age and mean square weighted deviation (MSWD). (b–d) The initial Nd isotopic composition of the samples calculated back to an age of 2,440 Ma plotted versus the La/Sm. The data points are colored by the probability that they belong to each of the suggested clusters (see color bar in the upper right).

intrusions in the Superior and Wyoming Cratons, are thought to be part of one of the oldest large igneous provinces on Earth (Ciborowski et al., 2015; Heaman, 1997).

Geochemical studies have shown that the parental melts to the lavas were komatiitic in composition and underwent ~50% fractional crystallization before eruption; they also originated from a long-term light rare earth element-depleted source (Puchtel et al., 1997, 2016). Their ages have been determined through Sm-Nd, Lu-Hf, Pb-Pb, and Re-Os whole rock isochron techniques, which all give slightly scattered isochrons with ages around ~2.4 Ga, suggesting that all of these isotopic systems have been relatively undisturbed since eruption (Puchtel et al., 1997, 2016). An isochron for the Sm-Nd system gives an age of $2,436.0 \text{ Ma} \pm 27 \text{ Ma}$ with an MSWD of 2.4. Combined rare earth element and isotopic data have also been used to show that the Vetreny belt lavas experienced ~4% contamination by preexisting crustal rocks on their way to the surface with the contaminants thought to be 3.1-Ga tonalites from the Vodla block (Puchtel et al., 2016). The well-constrained elemental and isotopic compositions along with well-understood petrogenesis and slightly scattered isochrons makes these excellent samples to test our mixture modeling approach and validate our results.

We applied our model to the Sm-Nd data set from Puchtel et al. (1997). We used a synthetic data set of 100 points to represent each analysis, including the analytical uncertainty, and ran 300 repetitions to allow the EM algorithm to converge. We modeled a mixture of one to five components within the Sm-Nd data set and allowed individual data points to belong to multiple isochrons. The model results are shown in Figure 5a for three components, the number suggested by the ICL parameter. However, the background plot shows linear scatter that is typical of nearly ideal isochrons. The model, though, subdivides the samples into three clusters, which at first pass seem arbitrary. However, by using the chemical data from Puchtel et al. (1997), we can evaluate the cluster subdivision and use this to show that the clusters suggested by the model

represent real differences in the data. Figures 5b–5d show how the model divides the data points between the clusters. Cluster 3, the largest cluster, contains the majority of the data that have intermediate La/Sm_N and intermediate initial Nd isotope composition. This cluster results in an isochron with the age and initial identical to Puchtel et al. (1997).

How the model assigns clusters 1 and 2 is distinctly different, but systematic. Cluster 1 is assigned an identical age to cluster 3 but has a slightly lower initial Nd isotope composition. Data assigned to this cluster represent samples with high La/Sm, indicative of crustal contamination. Additionally, cluster 2 is assigned a much younger age and higher initial Nd isotope composition, and the samples assigned to this cluster have the lowest La/Sm, which may represent secondary processes.

Though our model initially seems to divide the Vetreny data into arbitrary clusters some of which may not have age meaning, by comparing the outputs to other chemical information from the samples, we are able to further refine and interrogate the sample set. Instead of providing meaningless data, our method actually divides the Vetreny data set into very similar groups as were designated by the original authors, yet our model did so without any knowledge of the whole-rock trace element patterns that Puchtel et al. (1997) used. This highlights the potential of our modeling strategy to provide a sensitive technique for interrogating the detailed relationships between samples that are seemingly isochronous, or nearly so.

6. Cautions and Perspectives

The code for the model outlined above is freely available and is provided in the supporting information and can be used with any isochron isotope system (Lu-Hf, Re-Os, Rb-Sr, U-Pb, and U-Th) and is also easy to update to include new isochron systems (e.g., W-Hf or U-Pb in Tera-Wasserburg space). Despite our attempts to produce an unbiased model where the prior assumptions are laid out, there is potential for the model to identify clusters that have no geological meaning. The observation of scatter in isochron space does not necessarily imply that the data set is a mixture of multiple discrete components. Systematic measurement errors and poorly defined uncertainties can also create artificial isochrons. Therefore, we emphasize that the modeling strategy should be used with caution and the results be treated critically. Existing, independent knowledge must be incorporated into and compared with the modeling results before conclusions regarding the geological history of sample suites are arrived at (see our komatiite Sm-Nd example).

One of the major benefits of our modeling procedure is that the model individually assigns the probability that it belongs to each specific isochron to each of the data points. This methodology provides a new opportunity in the interpretation of mixtures in isotope data sets. This offers the potential to extract more valuable information from isochrons, leading to a better understanding of processes. This information can be used to guide further investigation where analysis of sample characteristics might be used to evaluate groupings extracted from our modeling procedure. As demonstrated in the examples we highlight, the presented modeling approach can be easily transferred to a variety of geological settings and used to statistically evaluate complex isochron data sets, ultimately leading to improved dating of geologic events. We foresee this approach being useful for the Re-Os system in oils, especially to determine if other samples retain age information from their source shales, which may increase understanding how isochrons are generated in oils, (see example in section 5). Also, we believe that our approach will be useful in U-Pb dating of minerals with high concentrations of common Pb that may be from variable sources, for example, carbonate or apatite dating and dating of meteorites, which often contain highly scattered data, for example, using the W-Hf and Rb-Sr systems, and it also has great potential in contaminated magmatic rocks. This technique is applicable to any isochron data set that involves discrete mixtures or samples that contain multiple initial isotopic sources. It should be noted, however, that strong overprinting of samples by secondary processes may remove the initial isotopic signatures. If there are no remnants of these primary signatures remaining in the samples, our model cannot recover them.

7. Conclusions

We have provided a description of a new method and associated code for treating scattered data as a discrete mixture of isochrons. The consideration that scatter may be represented by multiple isochrons is a new approach to treat such data and, importantly, does not violate the critical requirements for an isochron. Furthermore, the approach can be used to identify data that may belong to multiple isochrons and represent

mixtures in age or initial isotope composition space. Importantly, we ensure that the model does not overfit the data and does not attempt to fit multiple isochrons to data that are best represented as a continuous mixture. We demonstrate that the model can identify mixtures of isochrons and provide geologically meaningful results. These data classifications can then be independently verified by other techniques.

We test our method using two real examples of whole rock Sm-Nd Vetryny lava data (Puchtel et al., 1997) and Re-Os bitumen data from the Polaris MVT deposit in Canada (Selby et al., 2005). In the Sm-Nd example, we use our model to confirm the findings of Puchtel et al. (1997, 2016). Crucially, we statistically identify components within an Sm-Nd data set that are chemically distinct, and we show that our identified clusters represent samples that have either higher amounts of contamination, secondary alteration, or record pristine compositions. In the Re-Os bitumen example, we use a mixture of isochrons to explain scattered data with the youngest and oldest ages having real age significance and the other ages representing meaningless averages of these ages. The youngest age is consistent with the age for the deposit of ~360 Ma from independent age constraints, whereas the oldest age is similar to the age of the host sediments. This suggests that some component of the Re-Os system may not have been reset by the bitumen extraction event.

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References

- Baudry, J. P., Raftery, A. E., Celeux, G., Lo, K., & Gottardo, R. (2010). Combining mixture components for clustering. *Journal of Computational and Graphical Statistics*, 19(2), 332–353. <https://doi.org/10.1198/jcgs.2010.08111>
- Bertoletti, M., Friel, N., & Rastelli, R. (2015). Choosing the number of clusters in a finite mixture model using an exact integrated completed likelihood criterion. *Metron*, 73(2), 177–199. <https://doi.org/10.1007/s40300-015-0064-5>
- Biernacki, C., Celeux, G., & Govaert, G. (2000). Assessing a mixture model for clustering with the integrated completed likelihood. *IEEE Transactions on Pattern Analysis and Machine Intelligence*, 22(7), 719–725. <https://doi.org/10.1109/34.865189>
- Bikerman, M., Bowes, D. R., & van Breemen, O. (1975). Rb-Sr whole rock isotopic studies of Lewisian metasediments and gneisses in the Loch Maree region, Ross-shire. *Journal of the Geological Society, London*, 131(3), 237–254. <https://doi.org/10.1144/gsjgs.131.3.0237>
- Brooks, C., Hart, S. R., & Wendt, I. (1972). Realistic use of two-error regression treatments as applied to rubidium-strontium data. *Reviews of Geophysics*, 10(2), 551–577. <https://doi.org/10.1029/RG010i002p00551>
- Brooks, C., Wendt, I., & Harre, W. (1968). A two-error regression treatment and its application to Rb-Sr and initial Sr87/Sr86 ratios of younger Variscan granitic rocks from the Schwarzwald Massif, Southwest Germany. *Journal of Geophysical Research*, 73(18), 6071–6084. <https://doi.org/10.1029/JB073i018p06071>
- Chauvel, C., Dupre, B., & Jenner, G. (1985). The Sm-Nd age of Kambalda volcanic is 500 Ma too old. *Earth and Planetary Science Letters*, 74(4), 315–324. [https://doi.org/10.1016/S0012-821X\(85\)80003-0](https://doi.org/10.1016/S0012-821X(85)80003-0)
- Ciborowski, T. J. R., Kerr, A. C., Ernst, R. E., McDonald, I., Minifie, M. J., Harlan, S. S., & Millar, I. L. (2015). The Early Proterozoic Metchewan Large Igneous Province: Geochemistry, petrogenesis, and implications for Earth evolution. *Journal of Petrology*, 56(8), 1459–1494. <https://doi.org/10.1093/petrology/egv038>
- Cumming, V. M., Selby, D., Lillis, P. G., & Lewan, M. D. (2014). Re-Os geochronology and Os isotope fingerprinting of petroleum sourced from a type I lacustrine kerogen: Insights from the natural Green River petroleum system in the Uinta Basin and hydrous pyrolysis experiments. *Geochimica et Cosmochimica Acta*, 138(C), 32–56. <https://doi.org/10.1016/j.gca.2014.04.016>
- Davidson, J., Charlier, B., Hora, J. M., & Perleth, R. (2005). Mineral isochrons and isotopic fingerprinting: Pitfalls and promises. *Geology*, 33(1), 29. <https://doi.org/10.1130/G21063.1>
- Finlay, A. J., Selby, D., & Osborne, M. J. (2011). Re-Os geochronology and fingerprinting of United Kingdom Atlantic margin oil: Temporal implications for regional petroleum systems. *Geology*, 39(5), 475–478. <https://doi.org/10.1130/G31781.1>
- Finlay, A. J., Selby, D., & Osborne, M. J. (2012). Petroleum source rock identification of United Kingdom Atlantic margin oil fields and the Western Canadian oil sands using platinum, palladium, osmium and rhenium: Implications for global petroleum systems. *Earth and Planetary Science Letters*, 313–314, 95–104. <https://doi.org/10.1016/j.epsl.2011.11.003>
- Finlay, A. J., Selby, D., Osborne, M. J., & Finucane, D. (2010). Fault charged mantle-fluid contamination of U.K. North Sea oils: Insights from Re-Os isotopes. *Geology*, 38(11), 979–982. <https://doi.org/10.1130/G31201.1>
- Galbraith, R. F., & Laslett, G. M. (1993). Statistical models for mixed fission track ages. *Radiation Measurements*, 21(4), 459–470. [https://doi.org/10.1016/1359-0189\(93\)90185-C](https://doi.org/10.1016/1359-0189(93)90185-C)
- Gruau, G., Chauvel, C., & Jahn, B.-M. (1990). Anomalous Sm-Nd ages for the early Archean Onverwacht Group Volcanics. *Contributions to Mineralogy and Petrology*, 104(1), 27–34. <https://doi.org/10.1007/BF00310643>
- Hamdan, H., & Wu, J. (2013). Model selection with BIC and ICL criteria for binned data clustering by bin-EM-CEM algorithms. In *IEEE International Conference on systems, man, and cybernetics* (pp. 3133–3138). Manchester, UK: IEEE. <https://doi.org/10.1109/SMC.2013.534>
- Heaman, L. M. (1997). Global mafic magmatism at 2.45 Ga. Remnants of an ancient large igneous province? *Geology*, 25(4), 299–302. [https://doi.org/10.1130/0091-7613\(1997\)025<0299:GMMAGR>2.CO;2](https://doi.org/10.1130/0091-7613(1997)025<0299:GMMAGR>2.CO;2)
- Juteau, M., Michard, A., & Zimmermann, J. L. (1984). Isotopic heterogeneities in the granitic intrusion of Monte Capanne (Elba Island, Italy) and dating concepts. *Journal of Petrology*, 25(2), 532–545. <https://doi.org/10.1093/petrology/25.2.532>
- Kerr, J. W. (1977). Cornwallis Lead-Zinc District; Mississippi Valley-type deposits controlled by stratigraphy and tectonics. *Canadian Journal of Earth Sciences*, 14(6), 1402–1426. <https://doi.org/10.1139/e77-124>
- Leisch, F. (2004). Flexmix: A general framework for finite mixture models and latent glass regression in R. *Journal of Statistical Software*, 17, 1–18.
- Lillis, P. G., & Selby, D. (2013). Evaluation of the rhenium-osmium geochronometer in the Phosphoria petroleum system, Bighorn Basin of Wyoming and Montana, USA. *Geochimica et Cosmochimica Acta*, 118, 312–330. <https://doi.org/10.1016/j.gca.2013.04.021>
- Ludwig, K. R. (1991). Isoplot—A plotting and regression program for radiogenic isotope data. USGS Open-File Rept.91–445.
- Ludwig, K. R. (2003). User's manual for Isoplot 3.00: A geochronological toolkit for Microsoft Excel: Berkeley Geochronological Center Special Publication 4, 71.

- McIntyre, G. A., Brooks, C., Compston, W., & Turek, A. (1966). The statistical assessment of Rb-Sr isochrons. *Journal of Geophysical Research*, 71(22), 5459–5468. <https://doi.org/10.1029/JZ071i022p05459>
- McLean, N. M. (2014). Straight line regression through data with correlated uncertainties in two or more dimensions, with an application to kinetic isotope fractionation. *Geochimica et Cosmochimica Acta*, 124(0), 237–249. <https://doi.org/10.1016/j.gca.2013.08.035>
- Nicolaysen, L. O. (1961). Graphic interpretation of discordant age measurements on metamorphic rocks. *Annals of the New York Academy of Sciences*, 91(2), 198–206. <https://doi.org/10.1111/j.1749-6632.1961.tb35452.x>
- Okulitch, A. V., & Packard, J. J. (1986). Evolution of the Boothia Uplift, Arctic Canada. *Canadian Journal of Earth Sciences*, 23(3), 350–358. <https://doi.org/10.1139/e86-037>
- Powell, R., Hergt, J., & Woodhead, J. (2002). Improving isochron calculations with robust statistics and the bootstrap. *Chemical Geology*, 185(3–4), 191–204. [https://doi.org/10.1016/S0009-2541\(01\)00403-X](https://doi.org/10.1016/S0009-2541(01)00403-X)
- Puchtel, I. S., Haase, K. M., Hofmann, A. W., Chauvel, C., Kulikov, V. S., Garbe-Schönberg, C. D., & Nemchin, A. A. (1997). Petrology and geochemistry of crustally contaminated komatiitic basalts from the Vetreny Belt, southeastern Baltic Shield: Evidence for an early Proterozoic mantle plume beneath rifted Archean continental lithosphere. *Geochimica et Cosmochimica Acta*, 61(6), 1205–1222. [https://doi.org/10.1016/S0016-7037\(96\)00410-3](https://doi.org/10.1016/S0016-7037(96)00410-3)
- Puchtel, I. S., Touboul, M., Blichert-Toft, J., Walker, R. J., Brandon, A. D., Nicklas, R. W., Kulikov, V. S., et al. (2016). Lithophile and siderophile element systematics of the Earth's mantle at the Archean-Proterozoic boundary: Evidence from 2.4 Ga komatiites. *Geochimica et Cosmochimica Acta*, 180, 227–255. <https://doi.org/10.1016/j.gca.2016.02.027>
- Randell, R. N., & Anderson, G. M. (1990). The geology of the Polaris carbonate-hosted Zn-Pb deposit, Canadian Arctic Archipelago, current research, part D. *Geological Survey Canada*, 47–53(Paper 90–1 D).
- Savard, M. M., Chi, G., Sami, T., Williams-Jones, A. E., & Leigh, K. (2000). Fluid inclusion and carbon, oxygen, and strontium isotope study of the Polaris Mississippi Valley-type Zn-Pb deposit, Canadian Arctic Archipelago: Implications for ore genesis. *Mineralium Deposita*, 35(6), 495–510. <https://doi.org/10.1007/s001260050257>
- Selby, D., Creaser, R. A., Dewing, K., & Fowler, M. (2005). Evaluation of bitumen as a 187 Re-187 Os geochronometer for hydrocarbon maturation and migration: A test case from the Polaris MVT deposit, Canada. *Earth and Planetary Science Letters*, 235(1–2), 1–15. <https://doi.org/10.1016/j.epsl.2005.02.018>
- Symons, D., & Sangster, D. F. (1992). Late Devonian paleomagnetic age for the Polaris Mississippi Valley-type Zn-Pb deposit, Canadian Arctic Archipelago. *Canadian Journal of Earth Sciences*, 29(1), 15–25. <https://doi.org/10.1139/e92-003>
- Turgeon, S. C., Creaser, R. A., & Algeo, T. J. (2007). Re-Os depositional ages and seawater Os estimates for the Frasnian-Famennian boundary: Implications for weathering rates, land plant evolution, and extinction mechanisms. *Earth and Planetary Science Letters*, 261(3–4), 649–661. <https://doi.org/10.1016/j.epsl.2007.07.031>
- Vermeesch, P. (2010). HelioPlot, and the treatment of overdispersed (U-Th-Sm)/He data. *Chemical Geology*, 271(3–4), 108–111. <https://doi.org/10.1016/j.chemgeo.2010.01.002>
- Widom, E., Gaddis, S. J., & Wells, N. E. Jr. (2004). Re-Os isotope systematics in carbonates from Serpent Mound, Ohio: Implications for Re-Os dating of crustal rocks and the osmium isotopic composition of Ordovician seawater. *Geochemistry, Geophysics, Geosystems*, 5, Q03006. <https://doi.org/10.1029/2002GC000444>
- York, D. (1966). Least-squares fitting of a straight line. *Canadian Journal of Physics*, 44(5), 1079–1086. <https://doi.org/10.1139/p66-090>
- York, D. (1968). Least squares fitting of a straight line with correlated errors. *Earth and Planetary Science Letters*, 5, 320–324. [https://doi.org/10.1016/s0012-821x\(68\)80059-7](https://doi.org/10.1016/s0012-821x(68)80059-7)
- York, D., Evensen, N., Martínez, M., & Delgado, J. (2004). Unified equations for the slope, intercept, and standard errors of the best straight line. *American Journal of Physics*, 72(3), 367–375. <https://doi.org/10.1119/1.1632486>
- Zheng, Y. F. (1989). Influences of the nature of the initial Rb-Sr system on isochron validity. *Chemical Geology*, 80(1), 1–16. [https://doi.org/10.1016/0168-9622\(89\)90043-2](https://doi.org/10.1016/0168-9622(89)90043-2)