Supplementary Materials

Mass-Transfer and Fluid Flow along Extensional Detachment Faults in Hyperextended Rift Systems: The Examples of Tasna in the Alps, Mauléon in the Pyrenees, and Hobby High Offshore Iberia

Victor Hugo G. Pinto [1,*], Gianreto Manatschal [2], Anne Marie Karpoff [2], Emmanuel Masini [3], Rodolfo A. Victor [4], Adriano R. Viana [1] and Marc Ulrich [2]

Introduction

The following text briefly describe the mass balance method from Ague and Van Haren (1996) [72] used in our article. The main objective of this method is to calculate the gain and loss of elements or species with few samples. This is possible because the method contemplates the bootstrap procedure which creates virtual samples (or bootstrap samples) by averaging the real samples (i.e., laboratory samples) randomly. In addition, the protolith to altered rock transformation is better evaluated by the transformation between the bootstrap samples allowing creating a statistical distribution and the probabilities of loss and gain for each element or species. However, the reader may follow the Ague and Van Haren (1996) [72] article for a full comprehension of the method.

Gain and Losses of Elements Calculations

The gain (enrichment) and loss (depletion) of elements during mantle serpentinization and fault rock formation were calculated using the method proposed by Ague and Van Haren (1996) [72]. This method considers the mass and volume changes in metasomatically altered rock relative to the protolith. As a result, one has the time-integrated effect of all metasomatism that a given altered rock or suite of altered rock has undergone. The total mass change is given by Equation (1)

$$\frac{final\ mass - initial\ mass}{initial\ mass} = \left(\frac{C_i^o}{C_i'}\right) - 1 \quad (1)$$

where C is the concentration of immobile elements (i) in a protolith or original rock (o) and an altered rock ($'$). Volume strain (ε), results from mass gain or loss and changes in bulk density (ρ), as shown in Equation (2).

$$\frac{final\ volume - initial\ volume}{initial\ volume} = \left(\frac{C_i^o}{C_i'}\right)\left(\frac{\rho^o}{\rho'}\right) - 1 \quad (2)$$

From Equations (1) and (2), one has a positive value in case of mass gain or volume increase and a negative value for mass loss or volume decrease.

The total mass change of the mobile elements (j), τ, can be calculated from Equation (3) that expresses mass changes for j in terms of rock chemical, physical and volumetric properties.

$$\frac{final\ mass\ j - initial\ mass\ j}{initial\ mass\ j} = \left(\frac{\rho'}{\rho^o}\right)\left(\frac{C_j'}{C_j^o}\right)(\epsilon + 1) - 1 \quad (3)$$

This equation can be viewed in terms of the concentration of immobile elements substituting the volumetric strain from Equation (2) in Equation (3), as shown in Equation (4).

$$\frac{final\ mass\ j - initial\ mass\ j}{initial\ mass\ j} = \left(\frac{C_i^o}{C_i'}\right)\left(\frac{C_j'}{C_j^o}\right) - 1 \quad (4)$$

Two important points that cannot be forgotten when use this method, the concentration of an element cannot be zero and the sum of the elements needs to be 100 wt%. This is because zero concentration of any element will pose statistical issues, as we describe later.

Usually, the mass balance analysis assumes that volume strain and mass change have a normal distribution (Gaussian), but in reality, these distributions can be highly non-normal. Ague and Van Haren (1996) [72] show that assuming a normal distribution for compositional data can be misleading, especially when calculating mass balances. These authors use the so-called bootstrap method, which is essentially a Monte Carlo analysis that estimates the data distribution instead of assuming any a priori distribution. In addition, it can access confidence intervals for the results. Let $C_{n,m}$ be the concentration of the m-th constituent at the n-th sample. The bootstrap method consists of randomly choosing N samples and generating a new synthetic sample by averaging the original concentrations. For this, we use the Aitchison (1989) [98] Measure of Location (AML), shown in Equation 5,

$$(\bar{C}_1, \bar{C}_2, \ldots \bar{C}_M) = \frac{(g_1, g_2, \ldots, g_M)}{0.01 \sum_{m=1}^{M} g_m}, \quad (5)$$

where M is the total number of species and g_m is the geometric mean concentration of constituent m,

$$g_m = exp\left[N^{-1} \sum_{n=1}^{N} ln(C_{n,m})\right] \quad (6)$$

By repeating this experiment a number of times we can generate many synthetic data. In the random sampling, some of the original data can be absent or even appears more than once. Taking a dataset with 4 samples as an example, with the bootstrap method one can make thousands of simulations calculating the arithmetic mean, S(x), using a random sampling such as $S(x^{*1})=(x1+x3+x4+x4)/4$; $S(x^{*2})=(x2+x3+x3+x3)/4$ and $S(x^{*n})=(x1+x2+x3+x4)/4$, where x^{*n} is the n^{th} bootstrap sampling. The $S(x^{*1})$, $S(x^{*2})$,…, $S(x^{*n})$ will be new virtual samples. With this approach, one can have a reasonably fair statistical distribution, especially in studies with few samples (see Figure 1 from Ague and Van Haren, 1996) [72]. Therefore, the same idea can be applied to Equations (1)–(3), but rather than the arithmetic mean, we calculate the AML that is more suitable for multivariate compositional data (Aitchison, 1989) [98]. But as mentioned before, as we are dealing with the geometric mean, it cannot have zero values. We can now calculate the mass change using bootstrap

$$\hat{T}^* = \left(\frac{\bar{C}_i^o}{\bar{C}_i'}\right) - 1 \quad (7)$$

$$\hat{\tau}^{j*} = \left(\frac{\bar{C}_i^{o*}}{\bar{C}_i^{\prime *}}\right)\left(\frac{\bar{C}_j^{\prime *}}{\bar{C}_j^{o*}}\right) - 1 \tag{8}$$

where $\bar{C}$ is the AML calculated using Equation (5), and * indicates bootstrap samples. Volume change strain can be calculated using

$$\hat{\varepsilon}^{*} = \left(\frac{\bar{C}_i^{o*}}{\bar{C}_i^{\prime *}}\right)\left(\frac{\bar{\rho}_j^{o*}}{\bar{\rho}_j^{\prime *}}\right) - 1 \tag{9}$$

The bulk density ($\bar{\rho}$) is calculated using the arithmetic mean for both protolith and altered rock.

With the result of Equations (7) and (8), one can also have percentiles that is based on the data analysis instead of assuming a normal distribution. Therefore, the result can be expressed as a probability of mass and volume changes being loss or gain after a reaction.

The geochemical reference frame is another important point for the mass and volume calculations. It is important to know which elements are immobile to considered them as a reference. Usually, elements are discarded when they are part of altered minerals and veins, when there is a high variation among the samples, and when the results have large uncertainties related to analytical problems. Ague and Van Haren (1996) [72] suggest four ways to choose the reference frame. Option A: use the elements whose $\bar{C}_i^o/\bar{C}_i^{\prime}$ ratio is closest to the mean reference ratio

$$\widehat{mr} = g\hat{r}_i \tag{10}$$

where $g\hat{r}_i$ is the estimation of the geometric mean of the assumed immobile species' ratios. Option B: use the sum of the concentration of the chosen immobile species as a new one. For example, if one chooses TiO_2 and Al_2O_3, their sum will create a new species. For this option, we need to redo the normalization in Eq. 5. Option C: use the species whose $\bar{C}_i^o/\bar{C}_i^{\prime}$ ratio has the smallest confidence interval width. Option D: use Equation (9) directly in the mass balance equation and replace $\bar{C}_i^o/\bar{C}_i^{\prime}$ by $\widehat{mr}$ in Equations (7) and (8).

MacLean and Barrett (1993) [73] showed that elements such as Al, Ti, and Zr can be used as immobile species for many geological processes, including hydrothermal alteration. Immobility can be verified if these elements show a good linear correlation between selected protolith and altered rocks. This is the case for the samples we are analyzed as shown by Pinto et al. (2015) [4].