

On the Harker Variation Diagrams; A Comment on “The Statistical Analysis of Compositional Data. Where Are We and Where Should We Be Heading?” by Aitchison and Egozcue (2005)

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Abstract The current theoretical development of the analysis of compositional data in the article by Aitchison and Egozcue neglects the use of Harker’s variation diagrams and other similar plots as “meaningless” or “useless” on compositional data. In this work, it is shown that variation diagrams essentially are not a correlation tool but a graphical representation of the mass actions and mass balances principles in the context of a given geological system, and, when they are used correctly, they provide vital information for the igneous petrologist. The qualitative validity of the “spurious trends” in these diagrams is also shown, when they are interpreted in their proper geological framework. The example previously used by Rollinson to test the usefulness of the log-ratio transformation in the Aitchison and Egozcue article is revisited here in order to fully illustrate the proper use of this tool.

Keywords Compositional data · Variation diagrams · Lever rule · Mass balances · Mass actions

1 Introduction

Perhaps one of the fundamental aspects of mathematics is to seek universality and find a generic solution derived from particular problems/data. Due to this, it is not unusual that absolute statements are delivered by some authors, without taking fully into consideration (or understanding) some of the specific aspects of the particular applied problem under study. For instance, the statistical treatment of compositional data vs. a sensible interpretation of their trends has been a continuous argument between mathematicians and applied scientists (i.e., engineers, geologists). The contribution of Aitchison and Egozcue (2005) is a detailed summary of the former position,

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contributions like Baxter et al. (2005), Baxter and Freestone (2006) show the latter position. As an igneous petrologist, the author of this contribution is somewhat in between these two positions, i.e., dealing with applied compositional issues in very specific igneous petrology problems and trying at the same time to find a sensible and general statistical solution for them (i.e., Cortés et al. 2007). To date, it does not seem to be a general solution that can deal with both mass actions (i.e., trends and associations) and mass balances (i.e., conservation laws, Shurtz 2000, 2003), suggesting that different approaches have to be considered for different problems depending on their respective frameworks. In particular, the use or abuse of the well-known Harker or other variation diagrams has been a strong point of disagreement between these two groups, because this tool can be understood under both contexts, i.e., as mass action (which is being criticized), and as mass balances (i.e., the Lever Rule). It is not intended in this contribution to argue for or against the adequate statistics or geometry for a given context or framework, but rather to comment constructively on the particular bold condemnation of the variation diagrams published by Aitchison and Egozcue (2005) as a misleading geological tool. It will be shown here that the misconception begins with the erroneous attribution of these diagrams exclusively to be used in a mass action framework, and, more fundamentally, to the general fact that any interpretative petrological tool is meaningless without its geological context.

Harker's variation diagrams (Harker 1909) and diagrams similar to these (i.e., Fenner 1931), are binary plots, introduced exclusively for the study of the evolution of igneous rocks, in which two parts taken from a whole-rock chemical analysis are plotted, presented in a weight basis unit but without closing the parts (i.e., without normalizing the two plotted parts to 100%). In the particular case of the Harker's variation diagrams, major elements, reported in weight %, or minor elements, reported in parts per million or "ppm", are plotted against SiO_2 , also in weight %. Since the whole-rock chemical analysis (with all the parts) is closed to 100 wt.%, it is evident that any correlation between two of the parts is affected by the so-called spurious correlation effect (Pearson 1897), derived from the constant sum of the analysis (Chayes 1960, 1962; Aitchison 1982, 1986). For instance, in a variation Harker diagram of MgO wt.% vs. SiO_2 wt.%, typically a negative (spurious) correlation is observed between these two parts when an igneous system becomes more "evolved". Whilst the association between such variables is indeed positive since both components are being consumed by the growing solid phases, the crystallization of ferromagnesian minerals, in particular olivine (see example below), consume more MgO wt.% than SiO_2 wt.% during crystallization, producing the relative decrease of the former in relation with the latter.

Although it is agreed by the author that in a generic scenario, it is not always clear what "real" and what "spurious" correlations in a given set of variation diagrams are, the essential misconception here is to consider the diagrams out of their geological context, not to mention the fact that it is not the main purpose of them to find correlations between the plotted variables. From the Igneous Petrology perspective, there are three specific purposes in plotting compositional data using variation diagrams:

- (a) The simple display of the evolutionary trends shown by a related suite of magmas, in which such trends are consequence of crystal–liquid fractionation/assimilation processes, either partial melting, fractional crystallization or magma recharging

- (Wilson 1989; Cortés et al. 2005). These trends, spurious or not, are given by the law of Mass action (see below), have been well-known among petrologists for more than a century (Harker 1909), experimentally determined (Bowen 1928), thermodynamically modeled (Ghiorso and Sack 1995; Spera and Bohrsen 2004a, 2004b) and computationally simulated (Ghiorso and Sack 1995; Asimow and Ghiorso 1998). It is not expected to find the covariance structure associated with compositional data using these graphical trends, but rather interpret them within a given geological context.
- (b) Closely related with the previous objective is the fact that such trends, spurious or not, are the consequence of fairly known geological processes. It follows that the presence of a trend can be used as a robust evidence of the link between the samples if the geological processes are assumed. In particular, as a test of consanguinity of the samples (see below).
 - (c) Finally, from the point of view of a Mass balances framework, variation diagram can be used to quantitatively calculate the proportion of the species involved in the geological processes already assumed.

Thus, the essential difference between a compositional mathematician and an igneous petrologist is fundamental at the time of the interpretation of data. Whilst the compositional mathematician intends to fit the same model for the full composition or any relevant sub-composition, consistently and independently of the open or closed thermodynamic character of the system, for the igneous petrologist the goal is the identification of specific trends in the data and the calculation of the mass transferred associated with such trends, which were observed or simulated in the compositional space under the assumption of thermodynamic closeness.

2 Mass Action and Mass Balance

In a natural process, the chemical equilibrium, for instance, related with the crystallization of a given mineral phase, is governed by the law of mass action (Prigogine and Defay 1954). In other words, the concentration of reactants and products is controlled by an equilibrium constant that depends on equilibrium thermodynamics and the kinetic of the reaction (Lasaga 1998). Given a generic chemical reaction



in which the lowercases represent quantities and capital letters, chemical phases, the law of mass action can be expressed in terms of the equilibrium constant of the reaction

$$K(T, P) = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (2)$$

square brackets representing concentration or activities of the given phases. Therefore, when the system has reached equilibrium, there are very well defined proportions among reactant and product at a given pressure and temperature. Additionally, in terms of the kinetics of the reaction, an analogue constant can be defined, which

will govern the changes with time of the concentrations, defining pathways such as the liquid line of descent on the evolution of magmas.

A closely linked idea, but conceptually different, is directly derived from the conservation of mass principle. Thus, no matter the trend of evolution of the chemical reaction represented by (1), the amount of matter represented by reactants and products has to be conserved (Shurtz 2003).

These two related principles define the two conceptually different contexts in which chemical (in particular, geological) processes can be understood, both principles defining covariance structure and characteristic geometries. Simplicial geometry (Pawłowsky-Glahn and Egozcue 2006) seems to be the natural choice for a Mass Action context (as the log-ratio approach linearizes the equilibrium stated by (2)), Euclidean geometry for Mass balances (Shurtz 2000, 2003). For the particular case of variation diagrams, their validity hinges in the qualitative recognition of Mass Action patterns and the quantitative calculation of Mass Balances; in the following sections, both frameworks are explored.

3 The Evolution of a Magma Body

One of the main fields in the geological sciences is the study of igneous rocks and the mechanisms that produce such rocks, namely Igneous Petrology. It is beyond the scope of this brief work to give a detailed account on such broad subject; therefore, the reader is referred to general, introductory texts on the discipline such as Carmichael et al. (1974), Cox et al. (1979), Best (1989), Wilson (1989), Winter (2001). For the practical purposes of this contribution (i.e., what is expected to be found as a trend in a variation diagram), the main set of processes that can cause the evolution of a magma body and change its composition are the resultant of a fractionation/assimilation processes between magma and an “extract”. In most of the cases, the extract is a solid phase (i.e., crystals), whilst the remaining material is the molten phase (i.e., the magma). Among these processes, the most relevant are eruption (i.e., pure loss of material), magma recharge (i.e., new material added to the system), assimilation (i.e., material that comes from the magma chamber wall is added to the magma), and fractional crystallization (i.e., after crystals are formed, they are taken away from the magma). To simplify the argument, in the following discussion fractionation processes are explored, but the implications can be easily generalized for assimilation, or a combination of all such processes (Spera and Bohrson 2004a, 2004b).

Since what fractionates is taken from the melt, the framework for this family of processes is mass balance. Thus, and explicitly stating the obvious, the amount of matter in the solid phase (crystals) produced and fractionated from a magma given a process must be equal to the amount of matter subtracted from the magma used to generate the crystals. It is evident that, when an extract is fractionated from the melt, the absolute composition of such melt changes depleted in the components taken by the extract. But since the extract also takes the components in a given proportion as a composition in the mineral phases, the proportions of such components in the depleted melt will also change depending on what is being taken and in what proportion. The graphical expression of this principle is known as the Lever Rule.

4 The Lever Rule

In this section, the Lever Rule is presented for the particular case of a variation diagram as those proposed by Harker (1909) but the implications can be readily generalized, for instance, for ternary diagrams (Wilson 1989). Let there be a magma with a given composition in weight percent, from which a crystalline phase is being formed. Among the n -parts that represent the magma composition, let x_m and y_m be the proportions of parts x and y that are desired to be represented in a variation diagram. Analogously, the crystalline phase will take the parts x and y in the proportion x_c and y_c . Assuming that the total absolute amount of matter that forms the magma is M and the total absolute amount matter that forms the crystals is N , then, forming and fractionating such crystals will deplete the absolute amount of x and y in the magma by $(Mx_m - Nx_c)$ for x and $(My_m - Ny_c)$ for y . In order to calculate the new proportions of x and y in the now depleted magma, the new n -part composition has to be normalized by simply dividing by the total amount of matter present in the system after the fractionation of the crystals, i.e., by $M - N$.

It is clear that the points in a variation diagram representing the composition of the original magma (x_m, y_m) , the crystal (x_c, y_c) and the modified magma

$$\left(\frac{(Mx_m - Nx_c)}{(M - N)}, \frac{(My_m - Ny_c)}{(M - N)} \right) \tag{3}$$

are collinear in an Euclidean sense. In effect, it is straightforward to show that one of the points is on the Euclidean straight line defined by the other two points (see Appendix).

Having these three points forming an Euclidean straight line in a generic variation diagram, the relevance of the Euclidean distance or any other topologically equivalent metric becomes evident (i.e., Miller 2002). For instance, if the Extract is represented by “ E ”, the original magma composition by “ A ”, and the modified magma composition by “ B ”, then using the L1-norm, it can be shown that (see Appendix)

$$\frac{d_1(E, A)}{d_1(E, B)} = \frac{M - N}{M} \tag{4}$$

and

$$\frac{d_1(A, B)}{d_1(E, B)} = \frac{N}{M}. \tag{5}$$

In other words, for the particular case of a generic variation diagram (Fig. 1), the proportion between the fractionated extract and the proportion of evolved magma can be calculated, simply measuring the L1-norm lengths between A , B and E .

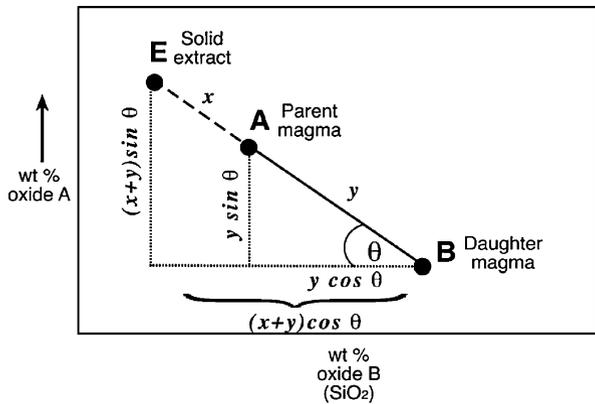
It can be also trivially shown for a variation diagram, that the canonical L2-norm equations (4) and (5) also hold true; from Fig. 1, it is evident that

$$\frac{d_1(A, B)}{d_1(E, B)} = \frac{y(\sin \theta + \cos \theta)}{(x + y)(\sin \theta + \cos \theta)} = \frac{y}{y + x} = \frac{d_2(A, B)}{d_2(E, B)}, \tag{6}$$

which means that the proportions between Extract, Parental magma and Daughter magma can be directly measured with a ruler in a plotted Harker diagram.

Fig. 1 The change in composition of parental magma (A) to daughter magma (B) in a variation diagram, given the crystallization of a solid phase extract (E). The whole process is controlled by the lever rule which can be used to calculate the proportions between the compositions (see text for details). Assuming that θ is the angle between the axes and the liquid line of descent

$d_1(E, A) = (x+y)(\sin \theta + \cos \theta)$
and $d_2(E, A) = (x+y)$



5 Example

In the following section, an example of Hawaiian basalts presented by Rollinson (1992) is revisited, mainly due to the fact that is quite well-known among compositional statisticians. The data correspond to 17 co-genetic analyses of basalts from Kilauea Iki lava lake, Hawaii, in which independent geological data demonstrated that olivine Fo₈₅ has fractionated the complete mineral chemistry composition not reported in Rollinson (1992). The most important result from a direct inspection of the data is the almost perfect ($R^2 = -0.997$) spurious inverse correlation found in these results, since the crystallization of olivine will consume both SiO₂ and MgO from the magma, hence, in absolute terms, both species will decrease. Since no chemical analysis of the composition of the olivine (Fo₈₅) is given in Rollinson (1992), solely to illustrate the procedure, a fairly similar (Fo₈₆) olivine chemical analysis was taken from the literature (Deer et al. 1997). In a real study, olivine mineral chemistry is determined from the samples by independent means rather than the whole-rock chemistry. Thus, the whole-rock chemistry compositional data and the mineral chemistry of this hypothetical co-genetic olivine are presented in the variation diagram MgO vs. SiO₂ (Fig. 2).

It has been shown in a previous section that the extraction of a fraction from the original magma generates an Euclidean straight pattern. In Fig. 2, estimations of such line are given using the least square regression of a straight line ($y = -3.730x + 193.584$), or a more consistent alternative with the L1-norm geometry, given by fitting a straight line $y = \alpha + \beta x$, minimizing (Sadovski 1974)

$$\sum_{i=1}^n |y_i - \alpha - \beta x_i|, \quad (7)$$

which gives the fairly similar line $y = -3.776x + 195.676$, due to $R^2 \sim 1$ (L1-norm fit is less sensitive to outliers than the usual Euclidean fit so it might be more adequate with noisy data). This particular mass action pattern can only be interpreted qualitatively as fractionation of olivine alone, because if a Mg-bearer new phase, typically pyroxene, begins fractionating from the magma after/during fractionation of olivine

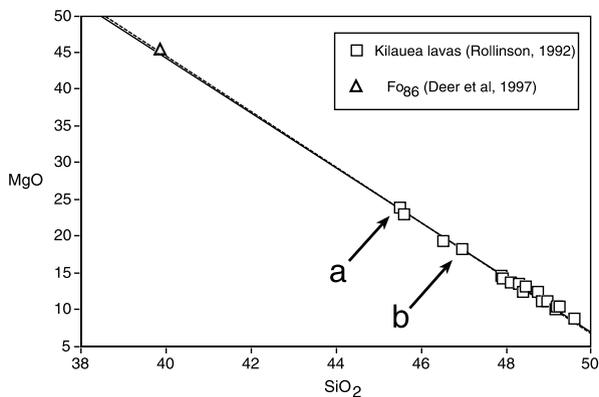


Fig. 2 MgO vs. SiO₂ variation diagram of Kilauea Iki lava lake from Rollinson (1992). Squares denote whole rock chemical analyzes, the triangle is a generic olivine analysis of an olivine Fo₈₆ taken from Deer et al. (1997). Solid line is the Least Absolute Value Regression of the data (cite) $\text{MgO} = -3.776 \times \text{SiO}_2 + 195.676$. Dashed line is a usual least square regression ($\text{MgO} = -3.730 \times \text{SiO}_2 + 193.584$). In both cases, the calculation included the olivine datum in the regression. For graphical measurements, the axes have to be drawn with the same proportions

then the trend will develop a “kink” and an inflection, changing the orientation of the evolution of the magma. As a motivating example, for further constructive discussion, the curved line observed in an igneous AFM ternary diagram (Kuno 1968; Irvine and Baragar 1971), which seems to resemble an “Aitchison straight line” (see, for example, Fig. 1 in Pawlowsky-Glahn and Egozcue 2006) is a consequence of shifting between two different mass action processes: the crystallization of olivine + pyroxene, followed by the crystallization of olivine + pyroxene + spinel in a tholeiitic magma. In fact, this inflection, when present, is the strict definition of a tholeiitic differentiation trend, whilst a more Euclidean straight-like trend defines the calc-alkaline differentiation trend in the same diagram (Kuno 1968).

Along the same lines, another use of variation diagrams is also a direct consequence of the mass action principle, based on the obvious fact that such linear patterns would be strongly associated with the liquid line of descent of the evolution of a single magma. Therefore, finding the patterns can nevertheless be only explained assuming consanguinity, which in the example means that all the samples in the set have different degrees of differentiation but the same magmatic origin. In the example, this is, of course, trivially known, but, in real complex applications, Harker diagrams are indeed a robust and cheap tool to assess similar origin and evolution of a magma suite.

From the point of view of the mass balances, not only phases (as pointed out, in this case olivine) can be determined using variation diagrams; the proportions between the extract and the melt can also be easily constrained using the lever rule, showing within this framework the “relevance” of the Euclidean (and equivalent) metrics. From the Rollinson (1992) example, we have selected and labeled in Fig. 2 the samples “a” and “b”. In Table 1, the proportions of SiO₂ and MgO of the samples and the olivine analysis taken from Deer et al. (1997) are given.

Table 1 SiO₂ and MgO parts for samples “a”, “b” and the generic olivine presented in Fig. 2. Data for the samples are from Rollinson (1992), data for the olivine is from Deer et al. (1997)

Sample	SiO ₂	MgO
olivine	39.87	45.38
“a”	45.5	23.87
“b”	46.96	18.31

Table 2 Taxicab distances between analyses

	olivine	“a”	“b”
olivine	0.00	27.14	34.16
“a”	27.14	0.00	7.02
“b”	34.16	7.02	0.00

Assuming that there is geological evidence that “a” is older than “b” and that the olivine given in Table 1 was found in the samples, then using the lever rule and the calculated distances presented in Table 2, it is possible to estimate that from a melt “a” 20.55% of the total mass of the system has been extracted to form phenocrysts of olivine, generating an evolved magma that represents the remaining 79.45% of the total mass of the parental magma. If, on the other hand, it is determined by any independent geological means that “b” is older than “a” then such amount of matter as phenocrysts of olivine is being added in the same calculated proportions to the system, which originally had the composition of “b”. This is normally interpreted as magma recharging with a more primitive (normally basaltic) batch of magma arriving to a magma chamber in which the resident magma has the more evolved composition.

6 Discussion and Conclusions

Thus, igneous petrologists and compositional statisticians arrive to the main predicament regarding compositional data. Under a mass balance context the geometry must be Euclidean. On the other hand, within the mass action framework, in order to find consistent correlations between the parts, the geometry has to be Aitchison’s because only the ratios carry the relative information expressed as compositions. As examples, in order to illustrate this dichotomy, we refer to Cox et al. (1979) in which it is shown that mass balance calculations performed in variation diagram are not possible when the diagram involves ratios between parts, or the fact that lever calculations are not possible if Aitchison’s metric (Aitchison et al. 2000) is used, whilst the negative association between MgO and SiO₂ in a Harker diagram is clearly spurious.

Therefore, the obvious question is what framework is more relevant in igneous petrology if not both to some extent. For the author of this contribution, it is clear from how long this argument has been active (almost five decades in the field of igneous petrology; Chayes 1960, 1962) that there is not a clear absolute answer for this predicament and the framework used will depend on the particular problem to be addressed. For the specific problem of variation diagrams, the mass balance framework is perhaps more relevant in terms of calculations (compare with the rather limited preliminary conclusions in Rollinson 1992), and yet there are qualitative uses of them

in the mass actions context, for instance, sometimes it is not straightforward to prove from a geological study whether the samples are genetically related or not. There are several analytical techniques that can be used to conclude such a relation, but the simplest (and cheapest) comes directly from interpreting in such qualitative way the variation diagrams: If the expected trends, spurious or not, are observed in a set of samples, then there are strong grounds to support the hypothesis that the samples are genetically related. Strongly linked with this concept is the evolution of the melt with the time involved in the process. For instance, the crystallization of a Mg-rich olivine (Mg_2SiO_4) in a basaltic magma consumes silica and magnesium in the molar proportion 1:2, which is reflected by the spurious negative correlation between silica and magnesium. Assuming in Fig. 2 that sample “b” is temporally older than sample “a” (measured by independent means), then, instead of fractionation of a crystalline phase, such a solid phase is being added to the melt, i.e., no fractional crystallization process has happened but magma recharging and mixing had (Cortés et al. 2005).

Regarding the example shown in the previous section, it has to be pointed out here that this is probably the simplest possible use of the technique. In a real study, variation diagrams are interpreted, considered as a whole set, and all the trends are analyzed together paying special attention to how all the elements vary together on the evolution of a geological system (Cortés et al. 2005). Thus, a very precise determination on the n-parts composition of what is being fractionated and how much can be easily calculated from the diagrams performing multiple simultaneous levers (for the interested reader, more elaborated examples can be found in Cox et al. 1979; Winter 2001). From their very beginning, variation diagrams were not intended to show correlations. In the words of Harker (1909), “We have premised that the analyzes plotted are those of rocks connected by a real serial relationship”, that is, it is assumed, based on additional independent geological data, that the trends shown in the diagrams are the result of processes that link the samples in their evolutionary history. Quoting Aitchison (2003): “compositions provide information only about the relative magnitudes of the compositional components and so interpretations involving absolute values as in the above example cannot be justified. Only if there is evidence external to the compositional information would such inferences be justified”, it is clear that Harker diagrams are then justified because either they are used assuming an external relationship (consanguinity) or with the premise that only the liquid line of descent on the evolution of a magma produces linear patterns. These aspects do not mean that statistical tools cannot be used as an aid in the interpretation of variation diagrams. In fact, two different kind of regressions were performed in order to find the straight lines shown in Fig. 2. It is also believable for the author of this contribution that simplicial geometry can be also used to interpret the mass action trends as a complement to any mass balance calculations, but more work needs to be done along these lines.

In summary, variation diagrams are a relatively cheap and easy visualization technique for geochemical compositional data, allowing quantitative calculations under the mass balances perspective and qualitative modeling under the mass action framework. Igneous petrologists have known this for more than a century, which is probably the reason why variation diagrams have survived the development of countless fancier new techniques in geochemistry and are always used as the first approach in

any petrological study. Thus, it is very likely that they will also survive the fierce efforts of the compositional statisticians trying to render them obsolete and meaningless as a petrological tool.

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Appendix: Some Relevant Proofs

Lemma 1 The points $P_B = (\frac{Mx_m - Nx_c}{M - N}, \frac{My_m - Ny_c}{M - N})$, $P_A = (x_m, y_m)$ and $P_E = (x_c, y_c)$ are collinear.

Proof An Euclidean straight line defined by points (x_m, y_m) and (x_c, y_c) has the form

$$y = \left[\frac{y_m - y_c}{x_m - x_c} \right] x + \left[\frac{x_m y_c - y_m x_c}{x_m - x_c} \right]$$

replacing x by the abscissa of point P_B

$$\left[\frac{y_m - y_c}{x_m - x_c} \right] \left[\frac{(Mx_m - Nx_c)}{(M - N)} \right] + \left[\frac{x_m y_c - y_m x_c}{x_m - x_c} \right] = \frac{(My_m - Ny_c)}{(M - N)}$$

which corresponds to the ordinate of P_B ; therefore, P_B, P_A and P_E are collinear. \square

Lemma 2 The L1-norm preserves the proportions of the mass transferred (The Lever Rule), i.e., using the same notation from Lemma 1

$$\frac{d_1(P_E, P_A)}{d_1(P_E, P_B)} = \frac{M - N}{M}$$

and

$$\frac{d_1(P_A, P_B)}{d_1(P_E, P_B)} = \frac{N}{M}.$$

Proof Is straightforward,

$$d_1(P_E, P_A) = |y_c - y_m| + |x_c - x_m|$$

and

$$d_1(P_E, P_B) = \left| \frac{Mx_m - Nx_c}{M - N} - x_c \right| + \left| \frac{My_m - Ny_c}{M - N} - y_c \right|,$$

which can be rearranged as

$$d_1(P_E, P_B) = \left| \frac{Mx_m - Nx_c - Mx_c + Nx_c}{M - N} \right| + \left| \frac{My_m - Ny_c - My_c + Ny_c}{M - N} \right|,$$

$$d_1(P_E, P_B) = \left| \frac{M(x_m - x_c)}{M - N} \right| + \left| \frac{M(y_m - y_c)}{M - N} \right|$$

since $M > N \Rightarrow \frac{M}{M-N} > 0$. Rearranging,

$$d_1(P_E, P_B) = \frac{M}{M - N} [|x_m - x_c| + |y_m - y_c|].$$

Equivalently, the proportion of extract will be

$$d_1(P_A, P_B) = \frac{N}{M - N} [|x_m - x_c| + |y_m - y_c|],$$

which proves the lever rule for the L1-norm. \square

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