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1	DOUBLE FIT: Optimization procedure applied
2	to lattice strain model
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36	the lattice strain model, KK implemented weighted fit and uncertainty propagation, R.
37	Dalou programmed and designed the user-interface, and R. Dennen helped design the

38 user-interface and the figures on the paper.

39

41 Abstract

42

43 Modeling trace element partition coefficients using the lattice strain model is a 44 powerful tool for understanding the effects of P-T conditions and mineral and melt 45 compositions on partition coefficients, thus significantly advancing the geochemical 46 studies of trace element distributions in nature. In this model, partition coefficients 47 describe the strain caused by a volume change upon cation substitution in the crystal 48 lattice. In some mantle minerals, divalent, trivalent, and tetravalent trace element cations 49 are mainly substituted in one specific site. Lattice strain model parameters, for instance in 50 olivine and plagioclase, are thus fit for one crystal site. However, trace element cations 51 can be substituted in two sites in the cases of pyroxenes, garnets, amphiboles, micas, or 52 epidote-group minerals.

53 To thoroughly study element partitioning in those minerals, one must consider the 54 lattice strain parameters of the two sites. In this paper, we present a user-friendly 55 executable program, working on PC, Linux, and Macintosh, to fit a lattice strain model 56 by an error-weighted differential-evolution-constrained algorithm (Storn, R., and Price, 57 K. 1997. Differential evolution - A simple and efficient heuristic for global optimization 58 over continuous spaces. Journal of Global Optimization 11, 341-359). This optimization 59 procedure is called DOUBLE FIT and is available for download on 60 http://celiadalou.wixsite.com/website/double-fit-program. DOUBLE FIT generates single 61 or double parabolas fitting experimentally determined trace element partition coefficients 62 using a very limited amount of data (at minimum six experimental data points) and 63 accounting for data uncertainties. It is the fastest calculation available to obtain the best-64 fit lattice strain parameters while accounting for the elastic response of two different sites 65 to trace element substitution in various minerals.

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67 Keywords: trace elements, partition coefficients, pyroxenes, lattice strain, fitting

68

69 1. Introduction

70

71 Elemental partition coefficients between Earth's phases are commonly employed to

72 interpret geochemical signatures of mantle-derived igneous melts and rocks. Because 73 trace element partitioning between equilibrated minerals an melts strongly depends on 74 their chemical compositions and the melting or crystallization pressure (P) and 75 temperature (T) conditions, trace element abundances in magmas can constrain the depth, 76 temperature, and extent of their partial melting in the mantle (e.g. Wood and Blundy, 77 1997; Wood et al., 1999; van Westrenen et al., 1999; Hill et al., 2000; van Westrenen et 78 al., 2000a,b; Salters et al., 2002; Bédard, 2007; Frei et al., 2009; van Kan Parker et al., 79 2010; Dalou et al., 2009, 2012; Cartier et al., 2014; Dygert et al., 2014; Bobrov et al., 80 2014; Michely et al., 2017). Therefore, partition coefficients (D) cannot be used as fixed 81 values in geochemical models, and understanding their variation with P-T conditions and 82 mineral and melt compositions is fundamental.

83 To do so, results of trace element partitioning studies are interpreted within the 84 framework of the lattice strain model (Blundy and Wood, 1994), which describes the 85 substitution parameters of elements in different crystal sites. In mantle minerals such as 86 olivine or plagioclase, divalent, trivalent, and tetravalent trace element cations are mainly 87 substituted in one site, respectively the M2 and M octahedral sites (Wood and Blundy, 88 2007). Lattice strain model parameters for those minerals are thus fitted for one crystal 89 site (M2 in olivine, e.g. Beattie, 1994; Taura et al., 1998; Zanetti et al., 2004; Lee et al., 90 2007; Michely et al., 2017; or M in plagioclase, e.g. Blundy and Wood, 1991; Bindeman 91 et al., 1998; Tepley et al., 2010; Sun et al., 2017). In contrast, trace element cations can 92 be substituted in both the M1 and M2 octahedral sites of pyroxenes and tri-octahedral 93 micas such as phlogopite and biotite, in the dodecahedral X site and the octahedral Y site 94 in garnet (sometimes possibly into its T site), in the three octahedral sites (M1, M2, and 95 M3), the distorted cubic M4 site, and the distorted cuboctahedral site A in amphiboles 96 (Wood and Blundy, 2007; Sun et al., 2018), and the 7- to 11-fold coordinated A1 and A2 97 sites in epidote-group minerals (Frei et al., 2003). Nevertheless, in many pyroxene-melt 98 partitioning studies (orthopyroxene, e.g. Green et al., 2000; Bédard, 2007, Lee et al., 99 2007; and clinopyroxene, e.g. Hill et al., 2000; Adam and Green, 2003, 2006; Gaetani et 100 al., 2003; McDade et al., 2003a,b; Bédard et al., 2014; Michely et al., 2017), cations in 101 the M1 site are not accounted for in the lattice strain model. Similarly, the lattice strain 102 model is often applied only to the X site in garnets (e.g. van Westrenen et al., 1999, 2000b; Green et al., 2000; Klemme et al., 2002; Adam and Green, 2003, 2006; Gaetani et
al., 2003; Pertermann et al., 2004; Corgne et al., 2004; Dalou et al., 2009). Others
consider multiple sites, but fit them separately in the lattice strain model (e.g. Adam and
Green, 2003, 2006; Dygert et al., 2014 for pyroxenes; Brenan et al., 1995; La Tourrette et
al., 1995; Dalpé and Baker, 2000 for amphiboles and phlogopites; and Frei et al., 2003
for epidote-group minerals), overlooking a possible relationship between the elastic
parameters of the two sites.

110 To apply the lattice strain model to both sites and fit experimentally determined 111 trace element partition coefficients, several approaches have been proposed. Frei et al. 112 (2009) and van Kan Parker et al. (2010) fit their experimental values using a weighted nonlinear least square Levenberg-Marquardt routine using the observed $D_i^{\text{opx-melt}}$ as a 113 weighting factor, and minimizing $\chi^2 = \Sigma [(D_i^{\text{observed}} - D_i^{\text{calculated}})^2 / D_i^{\text{observed}}]$ (Press et al., 114 1992). This method is limited as it is partly fitted by fixing some parameters. Cartier et al. 115 116 (2014) opted for a Monte Carlo-type approach; this brute-force method is more robust but 117 requires a large number of data and/or a long calculation time. In addition, both methods 118 did not account for data uncertainties.

119 In this paper, we present DOUBLE FIT, a lattice strain model fit by a differential-120 evolution-constrained algorithm (Storn and Price, 1997) adapted to be error weighted. 121 The optimization procedure generates double pseudo-parabolas fitting experimentally 122 determined trace element partition coefficients using a very limited amount of data (at 123 minimum 6 experimental data points, Fig. 1), is the first lattice-strain fitting program 124 accounting for measurement errors on data points, and offers the fastest calculation of the best-fit values for the lattice strain parameters of both pyroxene sites: r_0^{M1} , r_0^{M2} , E^{M1} , 125 E^{M2} , D_0^{M1} , and D_0^{M2} . 126

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128 2. Lattice strain models for pyroxenes

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At equilibrium, the dependence of trace element partitioning on the mineral composition attests to changes in the crystal structure (e.g. Blundy and Wood, 1994; see also the review by Blundy and Wood, 2003) when considering the crystal structure as an elastic body (Nagasawa, 1966; Brice, 1975). Substitution of a trace element cation for an 134 essential structural constituent of a crystal affects the lattice energetics of crystallographic 135 sites due to the misfit between the substituted cation and the essential structural 136 constituent whose radius is very close to the ideal radius of the site (Nagasawa, 1966; 137 Brice, 1975; Beattie, 1994; Blundy and Wood, 1994; Wood and Blundy, 1997). 138 According to their ionic radius and charge, elements are incorporated into different 139 crystal sites. Each site is characterized by the parameters of the lattice strain model 140 (Brice, 1975; Blundy and Wood, 1994). This model is based on the observation of a pseudo-parabolic relationship between cationic radii, r_i , and $\ln(D_i^{\text{crystal/melt}})$ values for 141 isovalent trace elements, *i* (Onuma et al., 1968), in which $D_i^{\text{crystal/melt}}$ is the Nernst 142 143 partition coefficient based on concentration ratios. This model, applied to the two pyroxene structural sites, is characterized by six parameters: r_0^{M1} and r_0^{M2} , the ideal 144 (strain-free) radii of the M1 and M2 sites, respectively; E^{M1} and E^{M2} , the elastic response 145 of the sites to the elastic strain caused by r_i different than r_0^{M1} and r_0^{M2} ; and D_0^{M1} and 146 D_0^{M2} , the fictive strain-free partition coefficients for the cations with r_0^{M1} and r_0^{M2} , 147 respectively. Following Frei et al. (2009), $D_i^{\text{crystal/melt}}$ regression to the lattice strain model 148 149 is expressed as:

150 $D_i^{crystal/melt} =$

$$151 \quad D_{o}^{M1} \exp\left(\frac{\alpha \cdot E^{M1}}{T} \left(\frac{r_{0}^{M1}}{2} (r_{i} - r_{0}^{M1})^{2} + \frac{1}{3} (r_{i} - r_{0}^{M1})^{3}\right)\right) + D_{o}^{M2} \exp\left(\frac{\alpha \cdot E^{M2}}{T} \left(\frac{r_{0}^{M2}}{2} (r_{i} - r_{0}^{M2})^{2} + \frac{1}{3} (r_{i} - r_{0}^{M2})^{3}\right)\right)$$
(1)

153 where *T* is temperature in Kelvin and $\alpha = \frac{-4\pi N_a}{R}$ with N_a the Avogadro constant and *R* 154 the gas constant.

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156 **3. Algorithms used to resolve the lattice strain models for 2 crystal sites**

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3.1 Previous work

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Previous works have used the nonlinear least square Levenberg-Marquardt algorithm (Frei et al., 2009; van Kan Parker et al., 2010). The Levenberg-Marquardt method often works well for nonlinear problems because they are guided by the geometry 163 of the objective function (e.g. the least square sum) in parameter space. However, in 164 many cases, this objective function may present many local minima. When there are 165 numerous minima, the algorithm becomes trapped in the first that it encounters. 166 Therefore, such algorithms are very sensitive to the initial set of parameters, which must 167 be very close to the optimized values if local minima are present.

The Monte-Carlo method, as used by Cartier et al. (2014), randomly generates a large number of possible solutions within a predefined range of lattice parameters. The best solutions are selected according to the deviation from experimental data. To limit the number of solutions and therefore the calculation, the solution domain (i.e. the range of parameters) must be restricted, either using literature data or "by eye" using experimental data for r_0^{M1} , r_0^{M2} , D_0^{M1} , and D_0^{M2} .

174 During global minimization, these methods are susceptible to failure in relatively 175 poorly-constrained situations, such as a minimization of six parameters with relatively 176 few data constraints. This is illustrated by mapping the residual surface of the systematic variation of r_0^{M1} , r_0^{M2} , E^{M1} , and E^{M2} to calculate D_0^{M1} and D_0^{M2} by simple matrix 177 inversion. Figure 2 is a contour plot of the uncertainty-weighted residual square surface 178 of E^{M2} versus r_0^{M2} , showing isolated local minima near the global minimum and a 179 gradient change at around $r_0^{M2} = 0.9$. Furthermore, we noted significant shifts of global 180 181 minima depending on the mapping resolution. These hidden issues of parameter fitting 182 lead to the publication of datasets that are often difficult to reconcile.

A solution to minimize these numerical problems is to use a global optimization
procedure, which explores a very large portion of the objective function landscape when
searching for the global minimum.

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3.2. Differential-evolution-constrained algorithm

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Compared to more classical "random search" methods, evolutionary algorithms (a form of global optimization) can be considered as "guided random search" algorithms. They are known as "evolutionary" because they take inspiration from natural evolution concepts like survival of the fittest, crossover, and mutation. In other words, more classical optimization methods consider a single best solution, whereas evolutionary 194 algorithms consider a population of candidate solutions; within that population, one 195 candidate is the best, but the others are kept as "samples" from which a better solution 196 can be found later. Therefore, evolutionary algorithms cannot be trapped at local optima 197 when a better solution can be found far from the current solution. Evolutionary methods 198 are thus extremely robust: they have an increased chance of finding a global or near 199 global optimum, are easy to implement, and are well suited for discrete optimization 200 problems. In the case of the lattice strain model, the global minimum must comply with 201 crystallographic requirements; therefore, crystallographic boundary conditions are 202 applied, reducing the parameter space.

203 Among the evolutionary methods, the differential evolutionary method is a 204 stochastic direct search method, which optimizes problems by iteratively trying to 205 improve a candidate solution based on a given quality criterion. This method has the 206 advantage of being easily "applied to experimental minimization where the cost value is 207 derived from a physical experiment" (Storn and Price, 1997). Applied to the lattice strain 208 model as the objective function $\mathcal{O}(\mathbf{p})$ (Eq. 1), we consider an experimental data set, accounting for uncertainties on the data, here one standard deviation of a set of 209 measurements, with N measured points $\mathscr{C}(r_i, D_i^{X/Y})$, where r_i is the ionic radius of 210 element *i* and $D_i^{X/Y}$ the partition coefficient between phases *X* and *Y*, with *i* = 1, 2,..., *N*. 211 The modeled data set, $\mathcal{M} = D_i^{X/Y}(r_i, \mathbf{p})$, is computed assuming a lattice strain model with 212 213 *n* continuous adjustable parameters $\mathbf{p} = \{\mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_n\}$. The simulated data set \mathcal{M} is then 214 compared to \mathcal{C} using the objective function $\mathcal{O}(\mathbf{p})$. The differential evolution algorithm 215 will attempt to find the optimal vector \mathbf{p} guided by $\mathcal{O}(\mathbf{p})$, starting with an initial 216 population of randomly generated parameter vectors which evolve during mutation, 217 cross-over, and selection cycles (Fig. 3), by minimizing two cost functions using the 218 Nash criterion (>0.9995) and the root mean square error (RMSE < 0.03). This evolution 219 reduces calculation time and can adapt to a very limited number of input experimental 220 data.

221 The DOUBLE FIT program can fit the lattice strain model with as few as six 222 experimental $D_i^{\text{px/melt}}$ values, and calculates the six model parameters. This is possible 223 because DOUBLE FIT accounts for the associated (and non-equal) errors on the data

values. Analytical constraints (interferences, analysis time, measurement accuracy) or the chemical system itself (e.g. the number of divalent and tetravalent cations is generally limited) often limit petrologists to selecting a limited number of elements to analyze, and thus a limited number of partition coefficients to fit (e.g., Fig. 1). To allow calculation of standard deviations on each lattice parameter, the DOUBLE FIT optimization runs 50 times. Calculation times vary between 20 and 40 s depending on the number of experimental data and the chosen parameter ranges.

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4. Description and use of the program

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DOUBLE FIT is an executable program written in the Python programming language and transformed as an executable (.app) available for download at <u>http://celiadalou.wixsite.com/website</u>. DOUBLE FIT runs on PC (64 bits only), Linux, and Macintosh, requiring only spreadsheet software to create a .csv data file. The input data files and variables can be entered directly in user-friendly windows following a straightforward procedure. DOUBLE FIT is thus easily accessible for users with no prior coding experience.

241 DOUBLE FIT provides four options:

- two options for a single fit procedure (one pseudo-parabola), for use
 with minerals where trace elements substitute in mainly one site (i.e.
 olivine and plagioclase), and
- two options for a double fit procedure applied to minerals where trace
 elements can substitute in two sites (i.e. pyroxene, garnet, micas, and
 epidote-group minerals).

For either the single or double fits, the program calculates the best-fit parameters based on the experimental data, and plots pseudo-parabolas. Published lattice strain parameters and partition coefficients can be specified for both the single and double fits to plot the pseudo-parabolas with the same formatting as figures output by the DOUBLE FIT optimization program. This option facilitates comparison between the DOUBLE FIT optimization and literature data.

- *4.1. Input data files*
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Experimental data are called from a .csv file as presented in Figure 4. Individual files must be created for divalent, trivalent, and tetravalent cations.

259 Cationic radii (first column, Ri) can be found in Shannon (1976) accounting for 260 the coordination of the substitution site of the studied mineral. For instance, as shown in 261 Figure 4 for trivalent cations, cations in orthopyroxene are in 6-fold coordination in both 262 octahedral sites, while in clinopyroxene, they are in 6-fold coordination in the M1 site 263 and 8-fold coordination in the M2 site. When only one substitution site is considered (e.g. 264 only Sc and rare earth elements, REE, are fitted for the trivalent cations), cations of 265 interest are 6-fold coordinated in the olivine M2 site, 8-fold coordinated in the garnet X 266 site or plagioclase A site, and 12-fold coordinated in the Ca-perovskite Ca site. However, 267 as cations can change coordination or substitution site depending on mineral composition 268 (e.g. Ba in amphiboles; Tiepolo et al., 2007) and/or their valence with oxygen fugacity 269 (e.g. Eu in plagioclase; Aigner-Torres et al., 2007; V, Cr, and Ti in pyroxenes; Cartier et 270 al., 2014), special attention should be paid when assigning ionic radii to each cation. For instance, to determine the proportion of Eu^{2+} versus Eu^{3+} , i.e. to recalculate $D_{Eu^{2+}}$ and 271 272 $D_{\text{Eu3+}}$, Aigner-Torres et al. (2007) used a rearranged version of the lattice strain model equation of Blundy and Wood (1994) in which D_0 and r_i are replaced respectively by the 273 measured partition coefficient and ionic radius of Sr to calculate D_{Eu2+} and of another 274 REE^{3+} (preferably Gd or Sm) for $D_{\text{Eu}3+}$, and $r_0^{(2+,3+)}$ and $E^{(2+,3+)}$ are fixed values taken 275 from Blundy and Wood (2003). This method allows fitting the recalculated D_{Eu2+} with 276 277 other divalent cations and the recalculated D_{Eu3+} with other trivalent cations.

278 The second column (D) of the data file corresponds to the measured partition 279 coefficients and the third column (eD) to their standard deviations. The minimum number 280 of data is six partition coefficients for the double fit options and three for the single fit 281 options. Although the fitting procedure works with these minimum numbers of data, if all 282 data are on the same side of the parabola, the fit will not reflect the true crystallographic 283 parameters. The ideal case to predict an accurate lattice strain model is to have data on each side of the r_0 value in the case of the simple fit and on each side of the r_0^{M1} and r_0^{M2} 284 285 in the case of the double fit.

The data file must be saved in .csv format, using "." for decimals and ";" for separation between columns.

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4.2 Procedure: example applied to clinopyroxene/melt partition coefficients

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We recommend saving the DOUBLE FIT program (__DOUBLE_FIT_m or w64__ folder) and data test files within the same directory. Once the executable file is started, it opens a terminal window and asks for the input data file path (Supplementary Fig. S1a), defaulting to a Data_test/CPX_test.csv location provided as an example. The second window asks for the experimental temperature in degrees Celsius (Supplementary Fig. S1b).

The third window (Supplementary Fig. S1c) allows the user to enter known parameters or continue with the full optimization procedure. Parameters must be entered in the correct units: E in Pa and r_0 in m. This option simply offers the possibility to compare lattice strain parameters obtained via another method in the same graphic output as our program. To continue with the full optimization procedure, users should proceed without entering any parameters (leaving the fields blank). The fourth window asks for the valence of the trace element to be fitted (Supplementary Fig. S2a).

To reduce the possibility of multiple solutions (and the optimization time), we propose a range of the D_0^{M1} , D_0^{M2} , E^{M1} , E^{M2} , r_0^{M1} , and r_0^{M2} parameters within which the optimization procedure searches for the best-fit parameters; this default range appears in the fifth window (Supplementary Fig. S2b) and changes depending on the valence of the trace elements (see Cartier et al., 2014). To reduce or extend the parameter ranges (and thus run time), new minima and maxima can be entered in the fifth window. If no values are entered, the optimization will continue with the default parameter ranges.

The procedure presented above also applies to the single fit procedure for singlesubstitution-site minerals. For the single fit option, the input data file path defaults to a SData_test/OL_test.csv location provided as an example for olivine/melt partition coefficients of trivalent cations. Additional examples of the double fit option, including partition coefficients of trivalent cations for orthopyroxene, amphibole, and garnet, are available for download at the same location. 317

- 318 4.3 Results
- 319

4.4 Limitations

320 After 20–40 s, results are available in the terminal (Supplementary Fig. S3a) and 321 in a results.txt file generated simultaneously. Graphical results are displayed another 2 s 322 later as a .png figure in a Python graphical window (Supplementary Fig. S3b). The figure 323 title includes the data file path and the run temperature of the sample. Best-fit parameters 324 with their standard deviations (after 50 iterations) are displayed on the figure. The figure 325 can be saved as .eps, .pdf, .ps, .svg, or .svgz for modification in vector graphical editors 326 for publication. Finally, users can continue using the same data file, select a new file, or 327 exit the program (Supplementary Fig. S3c) after closing the Python graphical window.

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331 The lattice strain parameters must be constrained to minimize the cost functions, 332 reduce run time, and avoid multiple convergence possibilities. We observe that when the parameter space is left very large (e.g. D_0^{M1} and $D_0^{M2} \in [0.001; 100]$ and E^{M1} and $E^{M2} \in$ 333 334 [100 ; 10000] GPa), statistical criteria are not satisfied, such as a subminimal Nash 335 criterion (<0.950), root mean square error (RMSE) >>1, errors on best-fit parameters 336 >100%, and/or a visually unsatisfactory fit.

337 Dalou et al. (2012) fit trivalent cations using the differential-evolution-constrained 338 algorithm (Storn and Price, 1997) via a primitive version of the DOUBLE FIT program, 339 and chose to minimize the cost functions using the Nash criterion (>0.9997) and RMSE < 340 0.04 while running the program in an acceptable time (maximum 30 s). To fulfill those 341 requirements, they constrained each parameter "with realistic boundary values" 342 (according to the accuracy of the measured data). The parameter space was defined to avoid *a priori* determination (e.g. $E^{M2} \in [100; 1000]$ GPa). However, in a few cases 343 344 when data uncertainties were too significant, especially on La, they choose to decrease the parameter space to allow convergence in a reasonable time (i.e. $E^{M2} \in [350; 430]$ 345 346 GPa).

These limitations arise directly from the differential evolutionary algorithm, which does not guarantee that a best-fit solution can be found. Here, for instance, when standard deviations on one or more $D_i^{X/Y}$ (i.e. on the experimental data $\mathcal{C}(r_i, D_i^{X/Y})$) are too large, the algorithm cannot minimize the cost function according to the criteria chosen (Nash criterion > 0.9997 and RMSE < 0.04). When this occurs, users can either discard experimental data with large uncertainties or reduce the parameter space.

Another limitation is that, because DOUBLE FIT was designed to run over a large parameter space, no convergence is possible if, on more than one experimental datum, errors exceed the partition coefficient values (D < eD). This generally applies to the largest most-incompatible cations such as La and Ce, which are quite difficult to measure in pyroxenes as they are at very low concentrations and their measurements are easily contaminated by surrounding melt. In that case, it may be best to discard very incompatible cation data to fit the lattice strain model.

360 Whereas for trivalent cations, a large number of trace elements are measured, 361 fewer, generally five or less, are typically measured for divalent (Ba, Pb, Sr, Ca, and Co) 362 and tetravalent cations (Th, U, Zr, Hf, and Ti), and by extension mono- and pentavalent 363 cations. This limitation can be overcome if the parameter space is reduced from the 364 default range, as shown on Fig. 5a for tetravalent cations. The addition of Mg and Ni data 365 in the M1 site allows using DOUBLE FIT for divalent cations (Fig. 5c). However, when 366 errors are large, it might be best to consider individually fitting the M1 and M2 sites 367 using the single fit option. For trivalent cations, the DOUBLE FIT program and the 368 weighted non-linear least square Levenberg-Marquardt routine (Frei et al., 2009) result in 369 equally good results (Fig. 5b).

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5. Example of application: Search for chemical equilibrium among orthopyroxene partitioning experiments

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Because most incompatible elements are concentrated in clinopyroxene rather than orthopyroxene, more mineral/melt partition coefficient data and lattice strain modeling are available for clinopyroxene than for orthopyroxene. One of the main reasons for this is the difficulty in accurately measuring low trace element concentrations in orthopyroxene. Another limitation lies in the capabilities of measuring trace element concentrations in orthopyroxene not contaminated by melt, implying very large orthopyroxene or a very small analytical beam (sometimes $<20 \,\mu$ m). The best example is La; the measured partition coefficient is often too large to represent the accurate La partition coefficient between mineral and melt (e.g. van Westrenen et al., 1999). In most cases, La is discarded from the dataset and not used to fit lattice strain models (Cartier et al., 2014).

385 One fundamental aspect of studying experimentally determined partition 386 coefficients is the attainment of chemical equilibrium. For major elements, one can use 387 textural observations (i.e. crystal shape), lack of compositional zoning in the crystal and 388 heterogeneity in the melt pool, the value of Fe-Mg exchange coefficients between 389 minerals and melts, or convergence of mass balance. For trace elements, most 390 experimental petrologists use the lattice strain models, arguing that if their trace element 391 partition coefficients can be plotted using the model then their partitioning data are near 392 chemical equilibrium. We suggest using this argument with caution, especially when the 393 experimental data are fitted with biases such as fixed parameters or narrow parameter 394 spaces. As shown on Fig. 5, multiple possibilities exist depending on the size of the 395 parameter space. This result is an outcome of any algorithm (not just DOUBLE FIT) 396 applied to the lattice strain model for a given data set. Decisions regarding the size of the 397 parameter space must be based on sound crystallographic knowledge to fully interpret the 398 lattice strain model: although interpretation of the lattice strain model provides hints to 399 partitioning data, it may not reflect equilibrium.

400 By calculating the energetics of ion substitution using atomistic simulation 401 techniques, Purton et al. (1996) obtained lattice strain parameters fitting trace elements 402 partition coefficients for CaO, diopside, orthoenstatite and forsterite. Without a reduced parameter space (especially for E^{M1} for the orthoenstatite), DOUBLE FIT is unable to fit 403 404 the Ni partition coefficients (Fig. 6a). This demonstrated the limitation of an empirical 405 model, without prior constraints on cation site assignment. Prior determination of the 406 main host cation for each site allows to reduce the parameter space for r_0 and to evaluate 407 each *E*, and guarantees a more accurate fit.

408	Finally, when many assumptions and constraints are applied to the lattice strain
409	fitting methods, even with data close to chemical equilibrium (Cartier et al., 2014),
410	extreme values can be obtained, especially for r_0^{M2} and D_0^{M2} . For instance, Cartier et al.
411	(2014) obtained very low r_0^{M2} for 3+ cations (0.66 to 0.79; Fig. 6b), which would imply
412	the absence of Ca and other large cations in the M2 site. In fact, the radius of the M2 site
413	in orthopyroxene is generally around 0.81–0.87 in this range of composition, i.e. Ca + Na
414	+ Mn = 0.15–1.1 wt% with Ca > Na >> Mn (Cameron and Papike, 1981). When the same
415	dataset is fit with DOUBLE FIT, only very incompatible cations do not obey the lattice
416	strain model, and best-fit lattice strain parameters (Fig. 6b) are more comparable to other
417	orthopyroxene/melt partitioning studies (i.e. Dalou et al., 2012; Frei et al., 2009).

418

419 Conclusions

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DOUBLE FIT applies a differential evolutionary algorithm (Storn and Price, solve the lattice strain model for two crystal sites when a limited number of experimental data are available. It is the fastest program to date applied to this model. It is designed to be user friendly and easily accessible for users with no prior coding experience.

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<u>Figure 1:</u> Example of the lattice strain model applied to experimentally determined partition coefficients between orthopyroxene and a basaltic melt for trivalent cations (sample F4p#3a, Dalou et al., 2012). The solid curve represents the fit of the lattice-strain model to $D_i^{Opx/melt}$, i.e. the sum of $D_i^{M1/melt}$ (dotted parabola) and $D_i^{M2/melt}$ (dashed parabola). Circles represent measured $D_i^{Opx/melt}$, i.e. the concentration of element *i* in orthopyroxene (opx) over the concentration of the same element in the equilibrated melt.



<u>Figure 2:</u> Contour plot of the uncertainty-weighted residual square surface of E_0^{M2} versus r_0^{M2} . To illustrate the subtle structure, the log of the residual value is shown:

$$\log(s^{2}) = \log\left(\frac{\sum \left(\frac{\ln\left(D_{observed}^{i}\right) - \ln\left(D_{modelled}^{i}\right)}{\delta_{D}^{i}}\right)^{2}}{\sum \left(\frac{1}{\delta_{D}^{i}}\right)^{2}}\right).$$

Note the presence of two small local minima, as well as the change of the gradient at around $r_0^{M2} = 0.9$. Because there are six parameters to solve for, it is impossible to visualize the true residual surface in a 2-D plot. The plot shown here is chosen to illustrate our point by picking a plane passing through the true global minimum of the mapped area. The two most varying parameters were chosen to define the plane.

Initial population of vectors p at the Gth-generation



Figure 3: Illustration of the mutation, cross-over, and selection processes of the differential evolutionary algorithm for $\mathbf{p} = 6$ parameters. See text for details.

ORTHOPY	ROXENE_e	xample.csv	CLINOPYROXENE_example.csv
Ri	D	eD	Ri D eD
1.032	0.003	0.001	1.016 0.054 0.018
0.947	0.026	0.001	1.066 0.273 0.006
0.938	0.048	0.001	1.053 0.323 0.027
0.901	0.102	0.002	1.015 0.467 0.006
0.861	0.187	0.004	0.977 0.461 0.010
0.745	0.873	0.009	0.745 1.213 0.017
0.615	5.606	0.042	0.615 6.543 0.020
0.535	0.374	0.032	0.535 0.376 0.173
OLIV	INE_exam	ple.csv	GARNET_example.csv
Ri	D	eD	Ri D eD
0.947	0.003	0.001	1.016 0.001 0.001
0.938	0.006	0.003	1.066 0.288 0.024
0.901	0.013	0.004	1.053 0.573 0.044
0.861	0.033	0.004	1.015 2.369 0.502
0.745	0.196	0.013	0.977 5.822 0.502
0.535	0.004	0.001	0.870 6.904 0.165

<u>Figure 4:</u> Example of the required data file format applied to orthopyroxene, clinopyroxene, olivine, and garnet. Note that no assumption is made in the data file of the location (M1 or M2 site) of the cations.



Figure 5: Example results of the DOUBLE FIT program using orthopyroxene/melt partitioning data of sample 2303-04-02 (Frei et al., 2009) for a) tetravalent cations, b) trivalent cations, and c) divalent cations. Depending on the size of the parameter space, DOUBLE FIT gives different results. With a reduced parameter space (D_0^{M1} min = 0.15, E^{M1} min = 2000, and E^{M2} max = 500), DOUBLE FIT fits the lattice strain model with five points for the tetravalent cations. However, with only Ba in the M2 site, DOUBLE FIT cannot properly fit the divalent data even when constrained with $D_0^{M2} \in [0.001; 0.01] E^{M2} \in [30; 100]$ GPa)



Figure 6: Comparison of the empirical fit of DOUBLE FIT (black curves) with methods fitting parameters a) E and r_0 (Purton et al. 1996), and b) E^{M1} and E^{M2} (Cartier et al. 2014) based on the energetics of ion substitution (dark grey curves in (a) and (b)). Cartier et al. (2014) determined D_0 and r_0 for the M1 and M2 sites by a Monte Carlo method. Light grey curves shows DOUBLE FIT model using the default parameter space.

- DOUBLE FIT applies to solve the lattice strain model for two crystal sites mineral.
- It uses a differential evolutionary algorithm (Storn and Price, 1997).
- It works even when a limited number of experimental data are available.
- It is the fastest program to date applied to this model.
- It is designed to be user friendly for users with no prior coding experience.

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