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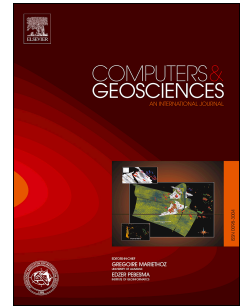
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# DOUBLE FIT: Optimization procedure applied to lattice strain model

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## Authorship statement

CD designed the DOUBLE FIT program and wrote the paper, JB wrote the original python code to adapt the differential evolutionary algorithm (Storn and Price, 1997) to the lattice strain model, KK implemented weighted fit and uncertainty propagation, R. Dalou programmed and designed the user-interface, and R. Dennen helped design the user-interface and the figures on the paper.

## 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.

66

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 and 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,

103 2000b; Green et al., 2000; Klemme et al., 2002; Adam and Green, 2003, 2006; Gaetani et  
104 al., 2003; Pertermann et al., 2004; Corgne et al., 2004; Dalou et al., 2009). Others  
105 consider multiple sites, but fit them separately in the lattice strain model (e.g. Adam and  
106 Green, 2003, 2006; Dygert et al., 2014 for pyroxenes; Brenan et al., 1995; La Tourrette et  
107 al., 1995; Dalpé and Baker, 2000 for amphiboles and phlogopites; and Frei et al., 2003  
108 for epidote-group minerals), overlooking a possible relationship between the elastic  
109 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  
113 nonlinear least square Levenberg-Marquardt routine using the observed  $D_i^{\text{opx-melt}}$  as a  
114 weighting factor, and minimizing  $\chi^2 = \Sigma[(D_i^{\text{observed}} - D_i^{\text{calculated}})^2/D_i^{\text{observed}}]$  (Press et al.,  
115 1992). This method is limited as it is partly fitted by fixing some parameters. Cartier et al.  
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  
125 best-fit values for the lattice strain parameters of both pyroxene sites:  $r_0^{\text{M1}}$ ,  $r_0^{\text{M2}}$ ,  $E^{\text{M1}}$ ,  
126  $E^{\text{M2}}$ ,  $D_0^{\text{M1}}$ , and  $D_0^{\text{M2}}$ .

127

## 128 **2. Lattice strain models for pyroxenes**

129

130 At equilibrium, the dependence of trace element partitioning on the mineral  
131 composition attests to changes in the crystal structure (e.g. Blundy and Wood, 1994; see  
132 also the review by Blundy and Wood, 2003) when considering the crystal structure as an  
133 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  
 141 pseudo-parabolic relationship between cationic radii,  $r_i$ , and  $\ln(D_i^{\text{crystal/melt}})$  values for  
 142 isovalent trace elements,  $i$  (Onuma et al., 1968), in which  $D_i^{\text{crystal/melt}}$  is the Nernst  
 143 partition coefficient based on concentration ratios. This model, applied to the two  
 144 pyroxene structural sites, is characterized by six parameters:  $r_0^{\text{M1}}$  and  $r_0^{\text{M2}}$ , the ideal  
 145 (strain-free) radii of the M1 and M2 sites, respectively;  $E^{\text{M1}}$  and  $E^{\text{M2}}$ , the elastic response  
 146 of the sites to the elastic strain caused by  $r_i$  different than  $r_0^{\text{M1}}$  and  $r_0^{\text{M2}}$ ; and  $D_0^{\text{M1}}$  and  
 147  $D_0^{\text{M2}}$ , the fictive strain-free partition coefficients for the cations with  $r_0^{\text{M1}}$  and  $r_0^{\text{M2}}$ ,  
 148 respectively. Following Frei et al. (2009),  $D_i^{\text{crystal/melt}}$  regression to the lattice strain model  
 149 is expressed as:

$$150 \quad D_i^{\text{crystal/melt}} =$$

$$151 \quad D_0^{\text{M1}} \exp\left(\frac{\alpha \cdot E^{\text{M1}}}{T} \left(\frac{r_0^{\text{M1}}}{2} (r_i - r_0^{\text{M1}})^2 + \frac{1}{3} (r_i - r_0^{\text{M1}})^3\right)\right) + D_0^{\text{M2}} \exp\left(\frac{\alpha \cdot E^{\text{M2}}}{T} \left(\frac{r_0^{\text{M2}}}{2} (r_i - \right.$$

$$152 \quad \left. r_0^{\text{M2}})^2 + \frac{1}{3} (r_i - r_0^{\text{M2}})^3\right)\right) \quad (1)$$

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.

155

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

157

#### 158 *3.1 Previous work*

159

160 Previous works have used the nonlinear least square Levenberg-Marquardt  
 161 algorithm (Frei et al., 2009; van Kan Parker et al., 2010). The Levenberg-Marquardt  
 162 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.

168 The Monte-Carlo method, as used by Cartier et al. (2014), randomly generates a  
169 large number of possible solutions within a predefined range of lattice parameters. The  
170 best solutions are selected according to the deviation from experimental data. To limit the  
171 number of solutions and therefore the calculation, the solution domain (i.e. the range of  
172 parameters) must be restricted, either using literature data or “by eye” using experimental  
173 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  
177 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  
178 inversion. Figure 2 is a contour plot of the uncertainty-weighted residual square surface  
179 of  $E^{M2}$  versus  $r_0^{M2}$ , showing isolated local minima near the global minimum and a  
180 gradient change at around  $r_0^{M2} = 0.9$ . Furthermore, we noted significant shifts of global  
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.

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

186

### 187 3.2. *Differential-evolution-constrained algorithm*

188

189 Compared to more classical “random search” methods, evolutionary algorithms (a  
190 form of global optimization) can be considered as “guided random search” algorithms.  
191 They are known as “evolutionary” because they take inspiration from natural evolution  
192 concepts like survival of the fittest, crossover, and mutation. In other words, more  
193 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,  
 209 accounting for uncertainties on the data, here one standard deviation of a set of  
 210 measurements, with  $N$  measured points  $\mathcal{E}(r_i, D_i^{XY})$ , where  $r_i$  is the ionic radius of  
 211 element  $i$  and  $D_i^{XY}$  the partition coefficient between phases  $X$  and  $Y$ , with  $i = 1, 2, \dots, N$ .  
 212 The modeled data set,  $\mathcal{M} = D_i^{XY}(r_j, \mathbf{p})$ , is computed assuming a lattice strain model with  
 213  $n$  continuous adjustable parameters  $\mathbf{p} = \{p_1, p_2, \dots, p_n\}$ . The simulated data set  $\mathcal{M}$  is then  
 214 compared to  $\mathcal{E}$  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  $D_i^{px/melt}$  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

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

231

#### 232 **4. Description and use of the program**

233

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

241 DOUBLE FIT provides four options:

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

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

254

255 *4.1. Input data files*

256

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

259 Cationic radii (first column,  $r_i$ ) 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  
271 instance, to determine the proportion of  $\text{Eu}^{2+}$  versus  $\text{Eu}^{3+}$ , i.e. to recalculate  $D_{\text{Eu}^{2+}}$  and  
272  $D_{\text{Eu}^{3+}}$ , Aigner-Torres et al. (2007) used a rearranged version of the lattice strain model  
273 equation of Blundy and Wood (1994) in which  $D_0$  and  $r_i$  are replaced respectively by the  
274 measured partition coefficient and ionic radius of Sr to calculate  $D_{\text{Eu}^{2+}}$  and of another  
275 REE<sup>3+</sup> (preferably Gd or Sm) for  $D_{\text{Eu}^{3+}}$ , and  $r_0^{(2+,3+)}$  and  $E^{(2+,3+)}$  are fixed values taken  
276 from Blundy and Wood (2003). This method allows fitting the recalculated  $D_{\text{Eu}^{2+}}$  with  
277 other divalent cations and the recalculated  $D_{\text{Eu}^{3+}}$  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  
284 each side of the  $r_0$  value in the case of the simple fit and on each side of the  $r_0^{\text{M1}}$  and  $r_0^{\text{M2}}$   
285 in the case of the double fit.

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

288

#### 289 *4.2 Procedure: example applied to clinopyroxene/melt partition coefficients*

290

291 We recommend saving the DOUBLE FIT program (\_\_DOUBLE\_FIT\_m or  
292 w64\_\_ folder) and data test files within the same directory. Once the executable file is  
293 started, it opens a terminal window and asks for the input data file path (Supplementary  
294 Fig. S1a), defaulting to a Data\_test/CPX\_test.csv location provided as an example. The  
295 second window asks for the experimental temperature in degrees Celsius (Supplementary  
296 Fig. S1b).

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

304 To reduce the possibility of multiple solutions (and the optimization time), we  
305 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  
306 optimization procedure searches for the best-fit parameters; this default range appears in  
307 the fifth window (Supplementary Fig. S2b) and changes depending on the valence of the  
308 trace elements (see Cartier et al., 2014). To reduce or extend the parameter ranges (and  
309 thus run time), new minima and maxima can be entered in the fifth window. If no values  
310 are entered, the optimization will continue with the default parameter ranges.

311 The procedure presented above also applies to the single fit procedure for single-  
312 substitution-site minerals. For the single fit option, the input data file path defaults to a  
313 SData\_test/OL\_test.csv location provided as an example for olivine/melt partition  
314 coefficients of trivalent cations. Additional examples of the double fit option, including  
315 partition coefficients of trivalent cations for orthopyroxene, amphibole, and garnet, are  
316 available for download at the same location.

317

318 *4.3 Results*

319

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.

328

329 *4.4 Limitations*

330

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  
333 parameter space is left very large (e.g.  $D_0^{M1}$  and  $D_0^{M2} \in [0.001 ; 100]$  and  $E^{M1}$  and  $E^{M2} \in$   
334  $[100 ; 10000]$  GPa), statistical criteria are not satisfied, such as a subminimal Nash  
335 criterion ( $<0.950$ ), root mean square error (RMSE)  $\gg 1$ , errors on best-fit parameters  
336  $>100\%$ , and/or a visually unsatisfactory fit.

337

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

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

353           Another limitation is that, because DOUBLE FIT was designed to run over a large  
354 parameter space, no convergence is possible if, on more than one experimental datum,  
355 errors exceed the partition coefficient values ( $D < eD$ ). This generally applies to the  
356 largest most-incompatible cations such as La and Ce, which are quite difficult to measure  
357 in pyroxenes as they are at very low concentrations and their measurements are easily  
358 contaminated by surrounding melt. In that case, it may be best to discard very  
359 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).

370

## 371 **5. Example of application: Search for chemical equilibrium among orthopyroxene** 372 **partitioning experiments**

373

374           Because most incompatible elements are concentrated in clinopyroxene rather  
375 than orthopyroxene, more mineral/melt partition coefficient data and lattice strain  
376 modeling are available for clinopyroxene than for orthopyroxene. One of the main  
377 reasons for this is the difficulty in accurately measuring low trace element concentrations

378 in orthopyroxene. Another limitation lies in the capabilities of measuring trace element  
379 concentrations in orthopyroxene not contaminated by melt, implying very large  
380 orthopyroxene or a very small analytical beam (sometimes  $<20\ \mu\text{m}$ ). The best example is  
381 La; the measured partition coefficient is often too large to represent the accurate La  
382 partition coefficient between mineral and melt (e.g. van Westrenen et al., 1999). In most  
383 cases, La is discarded from the dataset and not used to fit lattice strain models (Cartier et  
384 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  
403 parameter space (especially for  $E^{\text{M1}}$  for the orthoenstatite), DOUBLE FIT is unable to fit  
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**

420

421 DOUBLE FIT applies a differential evolutionary algorithm (Storn and Price,  
422 1997) to solve the lattice strain model for two crystal sites when a limited number of  
423 experimental data are available. It is the fastest program to date applied to this model. It  
424 is designed to be user friendly and easily accessible for users with no prior coding  
425 experience.

426

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428

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437

438

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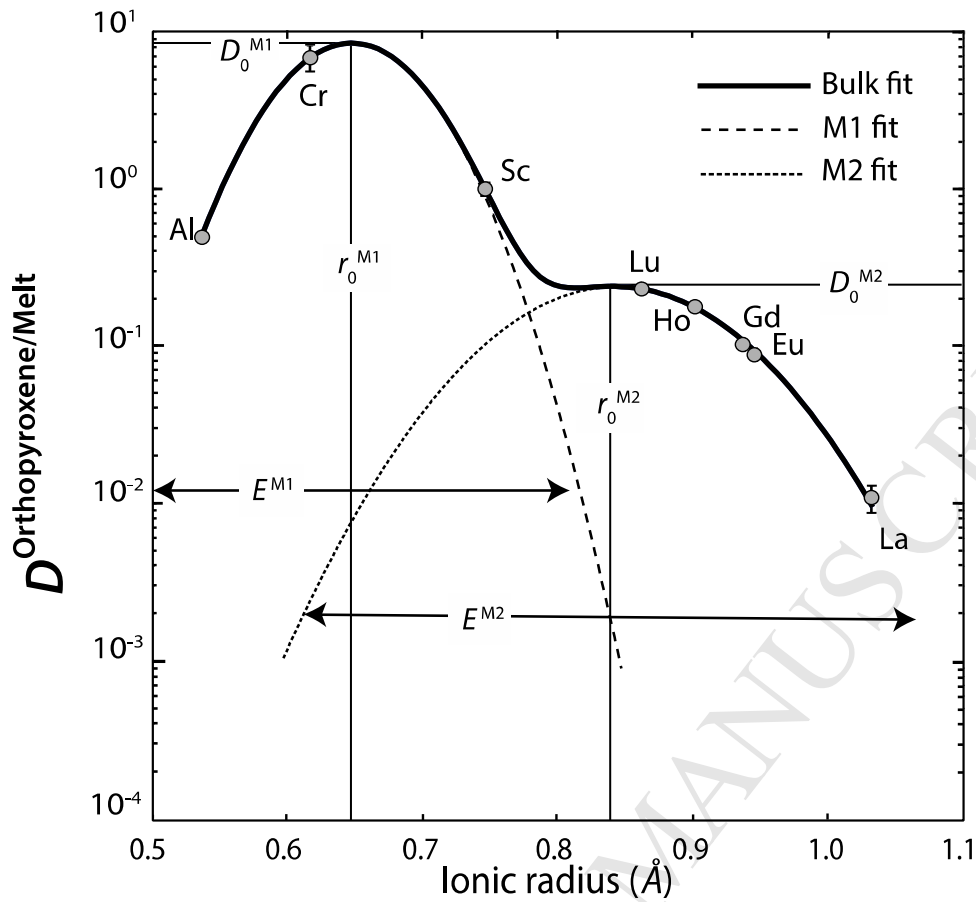
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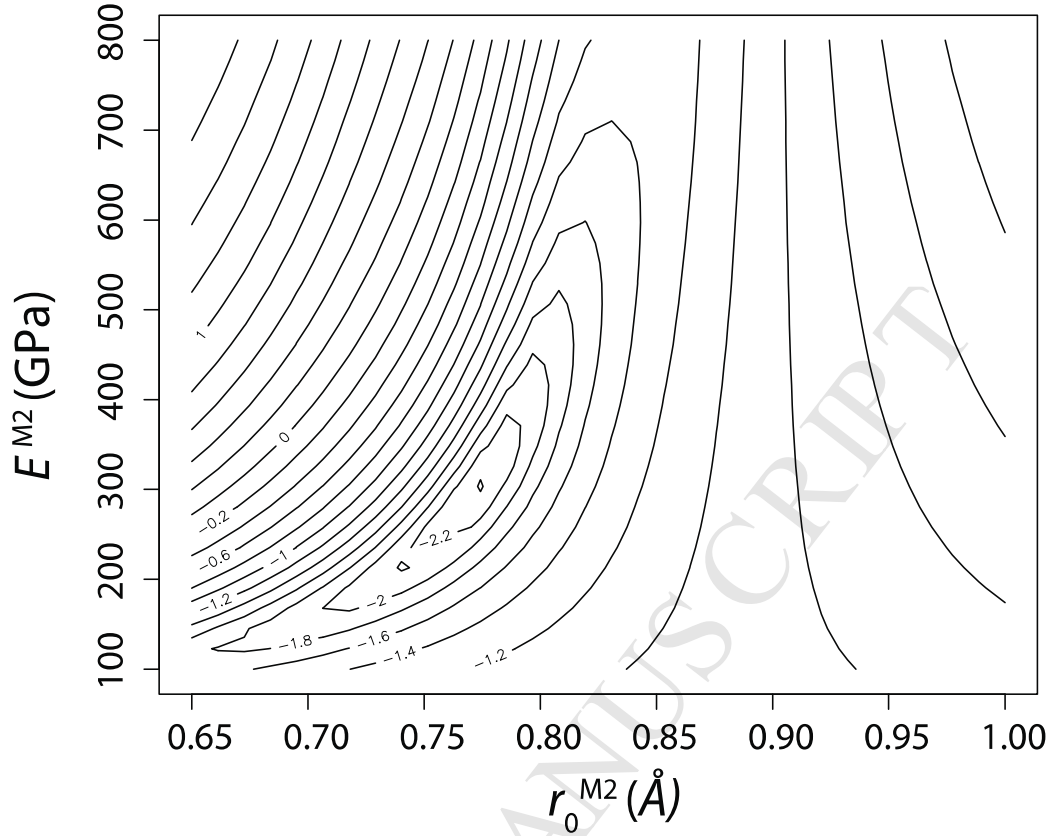
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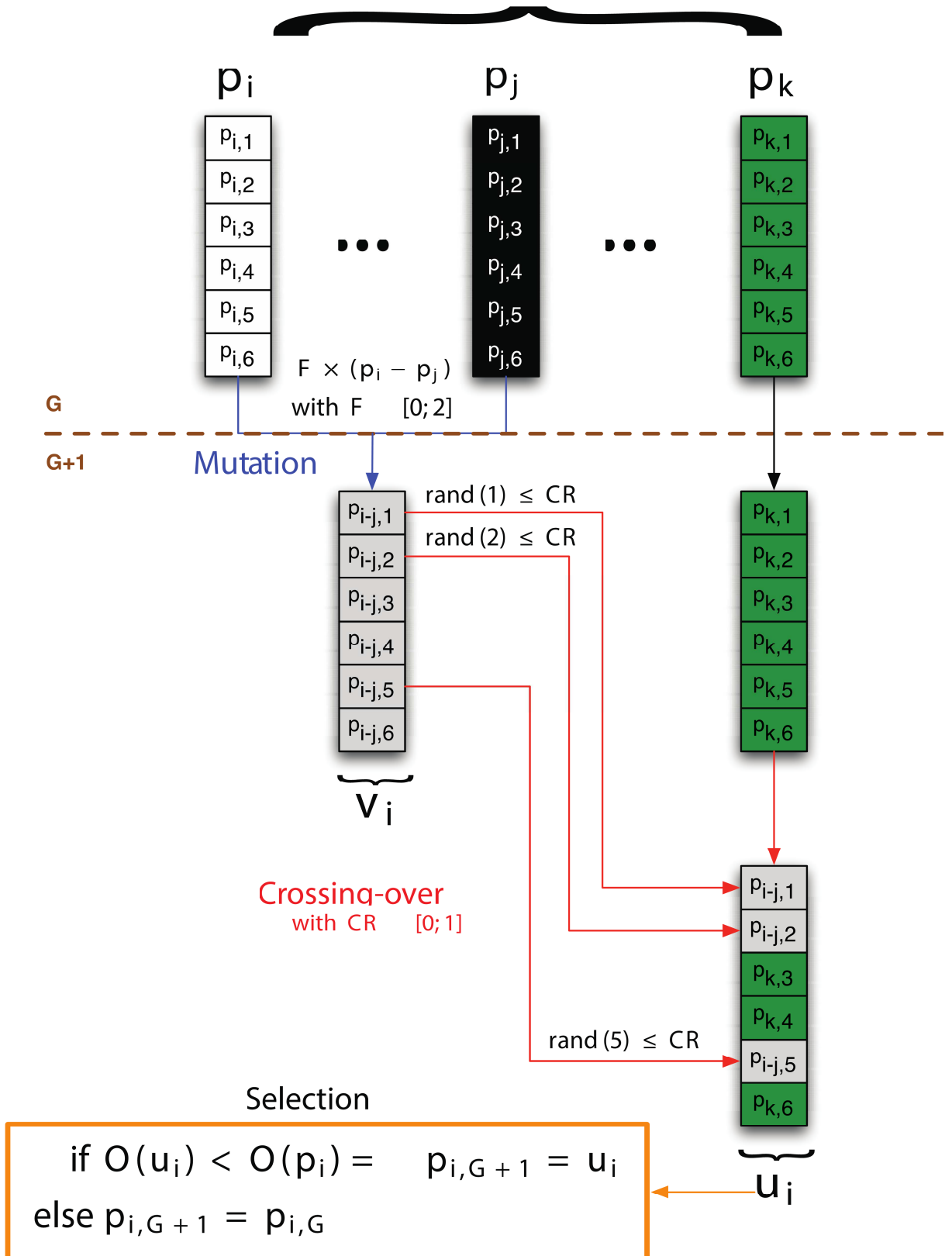
**Figure 1:** Example of the lattice strain model applied to experimentally determined partition coefficients between orthopyroxene and a basaltic melt for trivalent cations (sample F4p#3a, Dalou et al., 2012). The solid curve represents the fit of the lattice-strain model to  $D_i^{\text{Opx/melt}}$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



**Figure 2:** 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:

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

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  $\mathbf{p}$  at the  $G^{\text{th}}$ -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.

ORTHOPYROXENE\_example.csv

Ri	D	eD
1.032	0.003	0.001
0.947	0.026	0.001
0.938	0.048	0.001
0.901	0.102	0.002
0.861	0.187	0.004
0.745	0.873	0.009
0.615	5.606	0.042
0.535	0.374	0.032

CLINOPYROXENE\_example.csv

Ri	D	eD
1.016	0.054	0.018
1.066	0.273	0.006
1.053	0.323	0.027
1.015	0.467	0.006
0.977	0.461	0.010
0.745	1.213	0.017
0.615	6.543	0.020
0.535	0.376	0.173

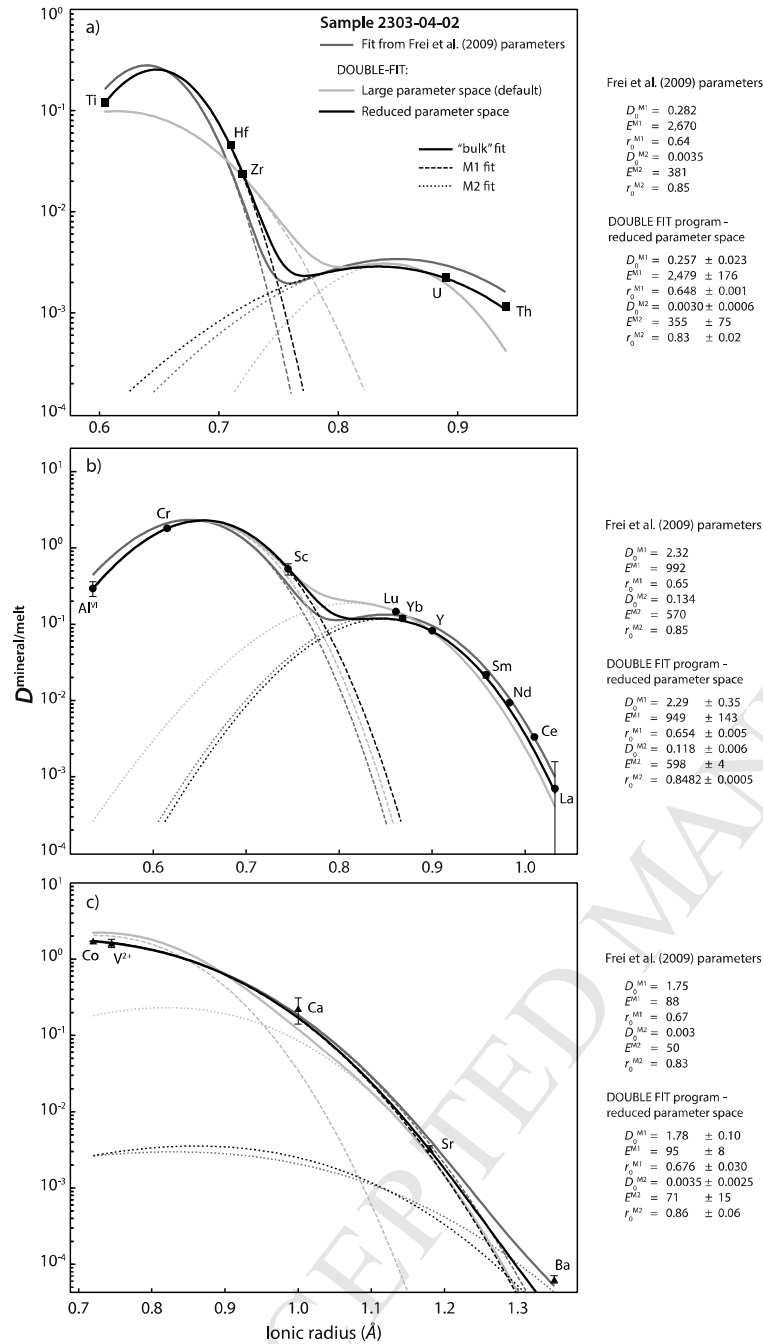
OLIVINE\_example.csv

Ri	D	eD
0.947	0.003	0.001
0.938	0.006	0.003
0.901	0.013	0.004
0.861	0.033	0.004
0.745	0.196	0.013
0.535	0.004	0.001

GARNET\_example.csv

Ri	D	eD
1.016	0.001	0.001
1.066	0.288	0.024
1.053	0.573	0.044
1.015	2.369	0.502
0.977	5.822	0.502
0.870	6.904	0.165

Figure 4: 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) tetraivalent 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 tetraivalent 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)

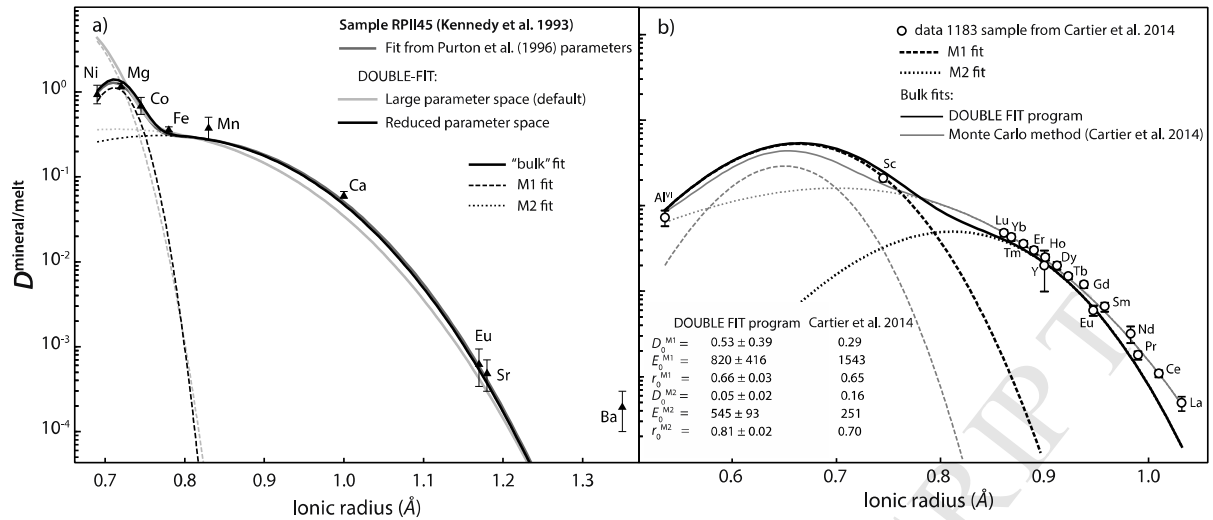


Figure 6: Comparison of the empirical fit of DOUBLE FIT (black curves) with methods fitting parameters a)  $E$  and  $r_0$  (Purton et al. 1996), and b)  $E^{M1}$  and  $E^{M2}$  (Cartier et al. 2014) based on the energetics of ion substitution (dark grey curves in (a) and (b)). Cartier et al. (2014) 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.