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1 **XMapTools: a MATLAB©-based program for**
2 **electron microprobe X-ray image processing and**
3 **geothermobarometry**

4

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24

25

26 **Abstract**

27

28 *XMapTools* is a *MATLAB*[®]-based graphical user interface program for electron
29 microprobe X-ray image processing, which can be used to estimate the pressure-
30 temperature conditions of crystallization of minerals in metamorphic rocks. This
31 program (available online at <http://www.xmaptools.com>) provides a method to
32 standardize raw electron microprobe data and includes functions to calculate the oxide
33 weight percent compositions for various minerals. A set of external functions is
34 provided to calculate structural formulae from the standardized analyses as well as to
35 estimate pressure-temperature conditions of crystallization, using empirical and semi-
36 empirical thermobarometers from the literature. Two graphical user interface
37 modules, *Chem2D* and *Triplot3D*, are used to plot mineral compositions into binary
38 and ternary diagrams. As an example, the software is used to study a high-pressure
39 Himalayan eclogite sample from the Stak massif in Pakistan. The high-pressure
40 paragenesis consisting of omphacite and garnet has been retrogressed to a
41 symplectitic assemblage of amphibole, plagioclase and clinopyroxene. Mineral
42 compositions corresponding to ~165 000 analyses yield estimates for the eclogitic
43 pressure-temperature retrograde path from 25 kbar to 9 kbar. Corresponding pressure-
44 temperature maps were plotted and used to interpret the link between the equilibrium
45 conditions of crystallization and the symplectitic microstructures. This example
46 illustrates the usefulness of *XMapTools* for studying variations of the chemical
47 composition of minerals and for retrieving information on metamorphic conditions on
48 a microscale, towards computation of continuous pressure-temperature-and relative
49 time path in zoned metamorphic minerals not affected by post-crystallization
50 diffusion.

51

52 **Keywords:** *XMapTools* program; X-ray chemical imaging; quantitative micro-
53 mapping; *PT*-maps

54

55

56 **1. Introduction**

57 Our understanding of the geodynamics and processes in orogens, subduction zones
58 and the lower crust relies on estimations of the pressure-temperature (*P-T*) conditions
59 of crystallization of mineral assemblages. Deriving reliable pressure and temperature
60 information from a rock is critical to our knowledge of the thermal structure of the
61 crust, whose variations can be recorded through time within individual samples via
62 consecutive partial re-equilibration events. Thermobarometric tools such as multi-
63 equilibrium thermobarometry (e.g. Berman, 1991), pseudosections (e.g. Holland and
64 Powell, 1998; 2011) and empirical thermometers (e.g. Cathelineau and Nieva, 1985)
65 provide these estimates from the nature and composition of minerals, even for high-
66 variance assemblages (Vidal and Parra, 2000). To shed light on the recrystallization
67 history of metamorphic rocks, chemical compositions of the minerals are required.
68 This is commonly achieved using point mode analyses obtained with an electron
69 probe microanalyser (EPMA). The use of X-ray images allows to identify the
70 relationships between microstructures, variations of composition and variations of *P-T*
71 conditions of crystallization (e.g. Vidal et al., 2006). Since the first X-ray “dot maps”
72 compositional image (Cosslett and Duncumb 1956), this technique has been
73 developed (see Friel and Lyman 2006 for a review) using both energy-dispersive and
74 wavelength dispersive X-ray spectrometers (EDS and WDS). For instance, previous
75 work has used X-ray images for classification and modal analysis (Launeau et al.,

76 1994; Bonnet, 1998; Cossio et al., 2002; Prêt et al., 2010) and to reconstruct *P-T* paths
77 (Kohn and Spear, 2000; De Andrade et al., 2006; Muñoz et al., 2006; Vidal et al.,
78 2006; Yamato et al., 2007; Ganne et al., 2012; Fiannacca et al., 2012; Lanari et al.,
79 2012; Plunder et al., 2012; Pourteau et al., 2013; Lanari et al., 2013). Quantitative
80 electron microprobe analyses require an analytical standardization of the number of
81 collected photons (X-ray intensity). The acquisition time for standardized point
82 analysis for eight major elements (e.g. Si, Al, Mn, Mg, Fe, Na, Ca, K) under classical
83 conditions (typically 10nA, 15keV, 40s) averages around two minutes. This approach
84 is therefore difficult to apply to chemical mapping, where samples are typically
85 heterogeneous on a ~10µm scale and maps typically contain about 150 000 pixels,
86 that would correspond to ~200 days of measurements. X-ray maps for quantitative
87 mapping can be obtained within a reasonable time frame by using a higher current
88 intensity and a lower counting time (100nA, 15 KeV, 100-300ms, see De Andrade et
89 al., 2006). In order to transform the X-ray intensities into calibrated weight
90 percentages, Clarke et al. (2001) used a Bence-Albee approach (Bence and Albee,
91 1968), which has been later implemented in the program XRMMapAnal (Tinkham and
92 Ghent, 2005). However, the precision of this standardization procedure is subject to
93 caution, because it can result in unreliable compositions for some geologically
94 important phases (e.g. quartz, muscovite, plagioclase and garnet, compositions listed
95 in the table 3 of Tinkham and Ghent, 2005). De Andrade et al. (2006) showed that
96 standardization of X-ray intensities using point analyses as internal standards
97 (Castaing, 1951) provides more reliable results.

98 In the present contribution, we present a *MATLAB*[®]-based Graphical User Interface
99 (GUI) program named *XMapTools* that can be used to: (1) classify mineral phases in
100 the sample, (2) convert X-ray intensities into calibrated weight percentages using

101 Castaing's approach, (3) calculate the structural formulae of the identified minerals,
102 (4) plot minerals compositions using various chemical diagrams, and (5) calculate P - T
103 conditions of equilibration using various empirical and semi-empirical
104 thermobarometers. An example of application of the program to a retrogressed
105 eclogite is presented below.

106

107 **2. Description of the program**

108 The *XMapTools* program (available at <http://www.xmaptools.com>) can be run with a
109 *MATLAB*[®] version 7.5 release R2007b or later. It uses a graphical interface named
110 *XMapTools.fig* (Fig. 1) built using the *MATLAB*[®] Graphical User Interface
111 Development Environment (GUIDE) tool. Each of the GUI components dragged with
112 the GUIDE is associated with a callback function in the program file *XMapTools.p*,
113 corresponding to a content-obscured version (encrypted executable).

114 The program is structured into three parts: *Xray*, *Quanti* and *Results* (Fig. 2)
115 corresponding to three different steps of the mapping process. The first step (*Xray*
116 column in Fig. 2), starts by loading the map. From statistical analysis of their
117 composition, pixels are grouped within mineral phases and possibly fractures or
118 voids, and corresponding masks are created. The user then identifies the nature of the
119 various groups. This step ends with the standardization stage. In the second step,
120 (*Quanti* column in Fig. 2), standardized maps are turned into maps of structural
121 formulae and into P - T maps. The last step (*Results* column in Fig. 2), allows the user
122 to produce binary and ternary chemical diagrams with the *Chem2D* and *TriPlot3D*
123 modules. All the functions used in these different stages are detailed below.

124

125 **2.1 Raw data treatment (Xray)**

126 Two types of datasets can be uploaded into *XMapTools*, namely the raw X-ray data in
127 photon counts per pixel (matrixes corresponding to the number of collected photons
128 per analyzed element per pixel) and the point analyses used as internal standards.

129 With both *Cameca*[®] and *Jeol*[®] EPMA, the raw data of chemical maps can be exported
130 in *ASCII* format text files such as **.txt* file. Typically, one file is created for each
131 measured element, and contains header lines reporting information about analytical
132 conditions and coordinates of the selected area, followed by a matrix of X-ray
133 intensity data (see Appendix 1). After removal of the header lines by the user, the
134 loading function of *XMapTools* reads the input files and creates X-ray intensity
135 images. This function includes dead-time correction, where the time interval after the
136 arrival of a pulse during which the spectrometer is unresponsive to further pulses
137 (Reed 2005) is accounted for, and transforms the measured counting rates into true
138 rates.

139 Point analyses, their coordinates and the map coordinates are the other required inputs
140 to the standardization step. Usually, the point analyses are made along different
141 transects at high angles to (mineral grain boundaries includes 'each other') mineral
142 grain boundaries to capture the total extent of the minerals heterogeneity. Experience
143 has shown that a minimum of 20 point analyses encompassing most of the chemical
144 heterogeneity of each mineral phases in the selected area of the sample is necessary to
145 reach optimum precision. The standard loading function reads a series of point
146 analyses. The locations of the point analyses must be carefully reported from stage
147 coordinates corrected for mechanical backlash and are then projected on the map with
148 the EMPA map coordinate system. The user can compare the X-ray intensities along
149 the profiles measured by point analyses to those of the map, which is useful to detect
150 problems of location of profiles on the map, for example due to drifting of the sample

151 stage during analysis or to a projection problem. The point analyses showing outlying
152 or unwanted compositions such as mixtures of fine minerals, inclusions, or grain
153 boundaries must be deleted before the standardization.

154

155 **2.1.1 Classification: mask creating function**

156 This function creates masks corresponding to entities identified in the map (e.g.
157 mineral, mineral boundaries, fractures), where each mask is a matrix of logical
158 numbers indexed on the coordinates of the composition map: the value of 1 is
159 attributed to the pixels belonging to a given mineral phase, and 0 to the other pixels.

160 This function allocates each individual pixel to one of the minerals phases. The mask
161 creating function uses the statistical analysis method K-means clustering to distribute
162 the pixels into groups of similar compositions. K-means identifies clusters and
163 allocates pixels to these clusters by minimization of the distance in compositional
164 space between the pixels and the gravity centre of each cluster (Saporta 1990).

165 The user selects one pixel of each phase on the chemical map as needed by the mask
166 creating function for initial guess. The compositions of these pixels are used as
167 starting cluster centroids. In an iterative loop, each pixel is assigned to the nearest
168 cluster and the centroids are recalculated until the sum of point-to-centroid
169 distances over all clusters is minimized (Seber, 1984; Spath, 1985). Two approaches
170 are available in *XMapTools*: the ‘normalized’ and the ‘classical’ approaches. Both of
171 them use a K-means clustering approach, but with different X-ray intensities inputs.
172 In the ‘normalized’ function, X-ray intensities of each element are normalized to their
173 mean values, with the result that all elements have the same weight and only the
174 variances are compared. In contrast, the X-ray intensities of each element in the
175 ‘classical’ method depend on the absolute concentration in each element. This

176 'classical' method is therefore more appropriate for elements present in high
177 concentration. Different masks may be derived using both methods, depending on the
178 magnitude of the differences between the compositions of the phases. An example is
179 shown in section 3.2. Other approaches for the classification of different mineral
180 phases can be found in the PetroMod program (Cossio et al., 2002). Here the K-means
181 algorithm was chosen for its straightforwardness and efficiency.

182

183 **2.1.2 Standardization function**

184 The analytical standardization consists in converting the measured X-ray intensities
185 into oxide weight percent concentrations using standards (Reed, 2005). The
186 standardization function performs this transformation for each mask where
187 quantitative information is available from point analysis or using user-defined
188 concentrations. The standardization of pixels requires calibration curves describing
189 how X-ray intensities change with concentration (Castaing, 1951). One calibration
190 curve is calculated for each element in each phase from the intensity versus
191 concentration relations constrained with point analyses. The calibration curves for Si
192 in the different phases of the studied sample are shown in Figure 3. For each mineral,
193 the calibration curve is a straight line between the origin (0 intensity and
194 concentration) and the central point of the cluster of the point analyses.

195 The standardization can be performed using one of the three methods available in
196 *XMapTools*. The first method 'Auto (median approach)' is fully automatic, and the
197 cluster centroids are the median values separating the higher half from the lower half
198 of the data. The 'Manual' approach allows the user to define the center of the clusters
199 and therefore the calibration curve. The last method 'Manual (homogeneous phase)' is
200 adapted to minerals assumed to be homogeneous such as might be the case for quartz.

201 The calibration curve is then defined as the mean value of X-ray intensity for the
202 selected mineral and the user enters the corresponding concentration, e.g. 100% for
203 SiO₂ in the case of quartz.

204

205 **2.2 Calculations from quantified data (Quanti)**

206 Once the masks have been defined and element concentrations have been estimated,
207 structural formulae may be calculated and equilibrium conditions derived using
208 external functions (see below). Users can add new thermobarometry or structural
209 formula functions. The file 'List-thermometers.txt' lists all information about these
210 external functions (i.e. category, name, input and output variables) that are stored into
211 the folder 'Functions'. All these functions are *MATLAB*[®] script m-files that can be
212 read and edited.

213

214 **2.2.1 Structural formulae functions**

215 Several structural formulae and atom site allocations models from the literature are
216 implemented in *XMapTools* (Table 1). A general function is also available to calculate
217 a structural formula normalized to a given number of oxygen atoms. This additional
218 function is used to compute the number of moles of elements per formula unit (p.f.u.)
219 for each pixel assuming that the total sums up to 100%.

220

221 **2.2.2 Thermobarometry functions**

222 *XMapTools* includes a large selection of thermobarometry functions based on
223 empirical and semi-empirical calibrations. These methods are distributed into two
224 groups: exchange reactions for thermometry (Table 2) and thermobarometer functions
225 (Table 3).

226 In exchange reactions, cations such as Fe^{2+} and Mg^{2+} are swapped between two
227 minerals (e.g. Spear, 1995). P - T conditions of equilibrium may be derived from the
228 cations partition between the two phases (e.g., Ravna, 2000a for garnet-
229 clinopyroxene). *XMapTools* generates an image with the oxide weight percent
230 compositions of the two minerals and allows the user to select pairs of pixels (spot
231 mode) or pairs of groups of pixels (area mode).

232 In the spot mode, the selected compositions are used to estimate the equilibrium
233 conditions. In the area mode, all the possible pairs of pixels are used to calculate an
234 average equilibrium condition with associated uncertainty. This mode allows to
235 propagate the effect of composition variation in any phase through the whole
236 thermobarometer calculation.

237 For exchange reactions, T is usually estimated for a given pressure. If the minerals
238 exhibit metamorphic zoning preserving paleo-equilibrium conditions, and if the
239 zoning pattern is not due to post-crystallization diffusion, the variations of T
240 conditions can be investigated using exchange reactions. A set of mineral pairs
241 selected between the core and the rim of two minerals provides a trend for the
242 evolution of the temperature conditions. This approach is essentially the same as
243 commonly used with point analyses.

244 The thermobarometry functions provide information on the T and/or P of mineral
245 crystallization for each pixel of the map, which can be turned into P , T , or P and T
246 maps. Both P and T conditions are derived from only one mineral composition (one
247 pixel) with fixed variables such as other mineral composition, or P or T . Methods are
248 listed in Table 3 in three groups: (1) thermometers, (2) barometers, and (3)
249 thermobarometers where P - T conditions are derived from at least two reactions (one
250 T -dependent and one P -dependent) within a given mineral assemblage. This is done

251 using groups of pixel compositions and assuming equilibrium between the groups.
252 The use of thermobarometry functions should be restrained to cases where the
253 relevant saturating assemblages are present in the studied sample. The functions
254 implemented in XMapTools do not check the presence of such assemblages because
255 some minerals may be outside the mapped area. This is then the responsibility of the
256 user to decide whether the functions can be applied to the studied sample.

257

258 **2.3 Chemical plots**

259 The mineral compositions or end-member proportions can be plotted as maps or into
260 chemical diagrams such as binary diagrams (Fig. 4a) using the *Chem2D* module, or
261 ternary diagrams (Fig. 5a) using the *Triplot3D* module. Both modules have a
262 graphical interface in which the user can select the plotted variables and manage the
263 diagram axes. A density plot function is also available to contour the analyzed
264 variables for density, which is useful when a large number of points is plotted as is the
265 case when working with maps (see examples in Fig. 4b and 5b). This function
266 displays a density map using the mineral composition data and grid spacing defined
267 by the user for density counting. The unit of the output of the density map is a number
268 of analyses per surface unit of the grid on the graph, which has the dimension of the x
269 axis multiplied to the y axis.

270 Two selection functions, namely ‘identify pixels’ and ‘multi-groups’, may be used to
271 select ranges of composition (rectangles) in the diagrams, as well as to identify the
272 selected pixels on the corresponding map (Fig. 4c and Fig. 5c) and to calculate modal
273 abundances.

274 Several functions may be used to create masks from user-defined chemical groups
275 within a phase. These masks are either built from manual selections (with the tools

276 “identify pixel” and “multi-groups”) or automatically using a K-means clustering
277 approach. The mask variable can be exported into ASCII format (*.txt file) and used
278 in the *Quanti* stage to export the average oxide composition corresponding to a
279 selection of pixels.

280

281 **2.4 Other functions**

282 All the results can be saved and previously saved projects can be loaded at any time
283 using the functions ‘save’, ‘save as’ and ‘load’. The save functions store the data in a
284 MATLAB© formatted binary file MAT-file (with .mat extension).

285 Functions in the ‘figure’ window are dedicated to the management of the color bar
286 such as setting the minimum and maximum values, the auto and reset buttons, and the
287 phase separator button (PhaseSep in Fig. 1). The user can also export the main figure
288 in usual image formats.

289 Functions in the ‘sampling’ window are used to select a subset of the data into the
290 main displayed image. These functions are available for any image (X-ray raw
291 measurement, map of oxide compositions, structural formulae, equilibrium conditions
292 maps). The selected data may be individual pixels, arrays or areas of pixels. This tool
293 can be used for example to draw the composition variations of a mineral grain along a
294 transect.

295

296 **3. Tests and evaluation**

297 Generating structural formulae and *P-T* maps from microprobe analysis is of interest
298 for petrology and geodynamics studies. In this section, we present an example of the
299 use of *XMapTools* on a metamorphic rock sample. Compositional maps were acquired
300 on an eclogite sample from the Stak area, a high pressure (HP) continental massifs in

301 NW Himalaya (Guillot et al., 2008; Lanari et al., 2013). This sample contains a well-
302 preserved eclogitic assemblage consisting of garnet and omphacite, which formed
303 during continental subduction. Omphacite was subsequently retrogressed to a Na-
304 poorer clinopyroxene + plagioclase + amphibole symplectite. The final metamorphic
305 event is recorded in the sample as a foliation comprising large crystals of amphibole
306 developed as a result of deformation and syntectonic hydration under mid-upper
307 crustal conditions (Lanari et al., 2013).

308

309 **3.1 Data acquisition**

310 An area of 0.348 mm² (520µm × 670µm) located in a symplectite zone and containing
311 garnet, clinopyroxene, amphibole, plagioclase, Ti- and Fe-oxides was mapped at the
312 Institute of Earth and Environmental Science, University of Potsdam, using a JEOL
313 JXA-8200 EMPA. Mapping conditions were 15 keV accelerating voltage and 100 nA
314 beam current, beam diameter smaller than 1 µm, 200 ms dwell time and 1 µm step
315 size (i.e. pixel size). X-ray intensities for Si, Ti, Al, Fe, Mg, Mn, Ca, Na and K were
316 measured in two passes.

317

318 **3.2 Classification**

319 An image of the mineral phases created using the ‘mask creating function’ (see §2.1)
320 is shown in Figure 6a. The two methods for the mask creating function (classical and
321 normalized) were tested and lead to similar estimates of the mineral modal
322 proportions except for garnet (Table. 4). The difference for garnet is due to the
323 erroneous allocation of the contour pixels around amphibole to the garnet mask when
324 using the classical approach. This artefact may be corrected by creating an additional
325 mask corresponding to the borders of the mineral or by using the normalized method.

326 Additional differences between the ‘normalized’ and ‘classical’ approaches are shown
327 in Figure 6b for a part of the map (dashed square in Fig. 6a). For instance, zone 1 in
328 Fig. 6b shows that omphacite is identified in the core of clinopyroxene using the
329 ‘normalized’ method only. This is due to the normalization procedure and originates
330 from the small chemical differences between omphacite and clinopyroxene in their
331 Na- and Mg-contents. These differences are not detected with the ‘classical’ method,
332 which allocates more pixels to the clinopyroxene mask. The other examples (2 and 3
333 in Fig. 6) show that in some cases, the opposite effect is observed when variations
334 occur in only one highly concentrated element, keeping effects of the variations in
335 low-concentrated elements to a minimum. From this, we conclude that the two
336 methods should be tested and we recommend to check the difference between the two
337 results and to compute different mask-files with different number of phases (including
338 the fractures and/or mineral boundaries).

339

340 **3.4 Test of the standardization**

341 Analytical standardization of the X-ray images was performed using the
342 ‘standardization function’ (see §4.1) with the ‘Auto (median approach)’ method.
343 Calibration curves (see §3.1 and graphical representation in Fig. 3) were calculated
344 for clinopyroxene, garnet, amphibole and plagioclase.

345 The quality and accuracy of the standardization can be investigated using the function
346 ‘Test of standardization’. This function plots the composition difference between
347 point analyses and the standardized composition on the same location on the maps. As
348 an example, the results for the standardization of garnet are reported in Fig. 8, which
349 shows that the pixel compositions derived from the standardized maps are in good
350 agreement, within analytical uncertainties, with the corresponding point analyses for

351 elements showing homogeneous compositions such as SiO₂, Al₂O₃, FeO (Fig. 8a, 8b
352 and 8c) and heterogeneous compositions due to zoning such as CaO, MgO and MnO
353 (Fig. 8d, 8e and 8f). In contrast, the point analyses of low concentration elements
354 TiO₂ and K₂O show trends not recorded in the standardized maps (Fig. 8g and 8h),
355 indicating that the concentrations of TiO₂ and K₂O mapped in garnet are not reliable,
356 because they are close to the detection limits for the used mapping analytical
357 conditions.

358

359 **3.5 Structural formulae and chemical study**

360 Clinopyroxene structural formulae were calculated on a 6 oxygen-basis by
361 distributing elements on tetrahedral (T1) and octahedral (M1, M2) sites. End-
362 members proportions of jadeite, diopside, hedenbergite, acmite and Ca-tschermak
363 (Table 1) were estimated according to the atom site allocation model of Spear (1995)
364 and Warren and Waters (2006). The amphiboles structural formulae were calculated
365 on a 23 oxygen-basis and elements were distributed on tetrahedral (T1, T2),
366 octahedral (M2, M13, M4), and 10 to 12-fold coordinated (A) sites. End-members
367 proportions of glaucophane, tremolite, tschermakite, pargasite, cumingtonite (Table 1)
368 were calculated according to the atom site allocation model of Dale et al. (2000;
369 2005). Structural formulae for garnet and plagioclase were respectively calculated on
370 a 12 and 8 oxygen-basis following classical atom-site allocation models (Table 1).
371 Structural formulae maps highlight the relationship between atom-site composition
372 and microstructures. The two chemical modules *Chem2D* and *Triplot3D* were used to
373 investigate the variations of clinopyroxene structural formulae (i.e. varying end-
374 member proportions). In Figure 4a, Na-rich clinopyroxene compositions were
375 selected (red dots) using the ‘identify pixel’ tool (§2.3) in the Na vs. Mg diagram. The

376 pixels belonging to the selected composition range are plotted in red on the map (Fig.
377 4c). These Na-rich clinopyroxene compositions are omphacitic and make up to ~25%
378 of the total clinopyroxene pixels. Then, clinopyroxene compositions were divided into
379 three groups using the 'multi-groups' tool within the jadeite-diopside-hedenbergite
380 ternary diagram (groups 1, 2 and 3 in Fig. 5a). The pixels belonging to the three
381 composition ranges are plotted on the map with corresponding colors (Fig. 5c). The
382 clinopyroxene compositions into the symplectite have lower Na contents,
383 corresponding to lower jadeite contents. Clinopyroxene-amphibole-plagioclase
384 symplectites are known to nucleate on grain boundaries between two omphacite
385 grains and to grow into the grain on one side, when the rock is sufficiently out of
386 equilibrium to nucleate the product (Joanny et al., 1991; Waters, 2002, 2003). In the
387 mapped area (Fig. 7), Na-rich clinopyroxene previously identified as omphacite
388 shows high Na contents (up to 0.4 p.f.u, zone 1 in Fig. 7). This primary omphacite
389 (width > 100 μ m) is destabilized into a first symplectite containing Na-poorer
390 clinopyroxene, plagioclase and amphibole. Clinopyroxene in this first symplectite
391 (zone 2 in Fig. 7) crystallizes as broad lamellae (30-40 μ m width) preserving the
392 original shape of omphacite, but with a lower Na-content (0.35 to 0.28 p.f.u.) than the
393 original omphacite grains. A second symplectite with the same minerals is observed
394 in zone 3 of figure 7, which shows smaller-size clinopyroxene lamellae (10-20 μ m
395 width) and Na-content (0.28 to 0.18 p.f.u.). Clinopyroxene lamellae are even smaller
396 in the last symplectite (width < 10 μ m) and also have lower Na-content (<15 p.f.u.).

397

398 **3.6 Precision and resolution**

399 In the previous section, maps of structural formulae highlight variations in the
400 clinopyroxene composition according to the symplectite microstructures. Na-content

401 in clinopyroxene decreases with decreasing size of the symplectite (i.e. with time).
402 The clinopyroxene solid solution includes jadeite while diopside hedenbergite and Ca-
403 tschermak are calcic end-members. As the multiplicity of the M2 site is one and
404 $X_{Fe^{3+}} = 0$ (corresponding to $X_{acmite} = 0$), the jadeite proportion is equal to the Na-
405 content in clinopyroxene. Estimating the uncertainties associated with the
406 compositional values of the structural formulae is needed before discussing the
407 implications linked to the chemical zoning.
408 The precision of the electron microprobe measurement with our experimental protocol
409 can be estimated using a Poisson law (De Andrade et al., 2006):

$$410 \quad p = \frac{2}{\sqrt{n}} \quad (1)$$

411 with p the precision (in % at 2σ), and n the number of recorded counts. The mean
412 intensities and precision measurements for each element (Si, Ti, Al, Fe, Mg, Ca, Na,
413 K) of clinopyroxene pixels are listed in Table 4. The precision measurements range
414 from 1.8% for Si to 20% for Ti. Uncertainties in the structural formula originating
415 from analytical errors were estimated using a Monte Carlo simulation where a total of
416 100 000 random clinopyroxene compositions were computed with a normal
417 distribution around the mean intensity compositions (Table 4) within 2σ of the
418 measured precisions. The standardization procedure was carried out for all the
419 compositions using the calibration curves estimated above. The average oxide
420 concentrations structural formulae and the associated standard deviations are listed in
421 Table 4. The average Na-content is estimated at 0.28 ± 0.03 p.f.u., which indicates
422 that the compositional variations identified above (ranging from 0.41 to 0.13) are
423 significant. It is emphasized that the uncertainties reported here are valid for the
424 present EPMA settings and range of clinopyroxene composition, and can be decreased
425 by increasing the dwell time.

426

427 **3.7 Combined *P* and *T* functions: *P-T* maps of Cpx**

428 *P-T* maps were built using combined *P* and *T* functions available in *XMapTools*
429 (description in §4.2 and list in Table 2). At the thin section scale, two assemblages
430 involving clinopyroxene are in equilibrium: the HP assemblage made of garnet,
431 omphacite and phengite (as inclusions in garnet, not present in the mapped area) and
432 the retrogressed assemblage represented by the clinopyroxene-plagioclase-amphibole
433 symplectite. These two parageneses were treated separately.

434 For the HP assemblage, *P-T* conditions for clinopyroxene pixels were estimated using
435 the *XMapTools* function ‘Cpx-P-T Rav (Omp-Gar-Phg)’. *P* was estimated using the
436 garnet, omphacite and phengite geobarometer of Waters and Martin (1993) and
437 Waters (1996). *T* was estimated using the garnet and omphacite geothermometer of
438 Ravna (2000a). The function estimates first T_1 at a given *P* (P_{input}), and recalculates
439 T_{n+1} and P_{n+1} until convergence (respectively 5°C and 0.1 kbar) between T_n and T_{n+1}
440 and P_n and P_{n+1} . As the compositions of garnet show a slight zoning (Alm₄₈ Prp₃₂₋₃₃
441 Grs₁₇₋₁₉ Sps₁), two average garnet compositions were defined, one for the core and
442 one for the rim (Lanari et al., 2013). In both groups, garnet compositions are
443 homogeneous within errors. Each pixel of omphacite was assumed in equilibrium
444 with one garnet average composition (core-core, rim-rim). Then, *P-T* estimates were
445 calculated for all omphacite compositions.

446 For the symplectite, *T* was first estimated using the edenite-richterite calibration
447 (Holland and Blundy, 1994) with the composition of amphibole pixels for a fixed
448 composition of plagioclase (function ‘Amp-T, Holland and Blundy 1994a’).
449 Crystallization *T* for amphibole were found to vary from 680±6°C in contact with
450 Jd_{30%} clinopyroxene to 640±8°C in contact with Jd_{10%} clinopyroxene. This

451 relationship was used to calculate the T of clinopyroxene. P for clinopyroxene
452 crystallization were subsequently calculated using the calibration of Waters (2003) for
453 the equilibrium reaction: $\text{jad} + \text{trem} = \text{alb} + \text{ed}$.

454 About 165 000 P - T calculations (one for each Cpx pixels) have been obtained and the
455 results have been plotted into binary diagrams (Fig. 9a and 9b) using the module
456 Chem2D, and into P and T maps (Fig. 9c and Fig. 9d). The density P - T diagram
457 option (Fig. 9b) plotted using the Chem2D module shows that the apparent deviation
458 in P is composed of a small proportion of points ($< 1\%$). In contrast, the density
459 diagram shows a significant trend for T and P corresponding to the prograde evolution
460 from 650°C to 750°C and from 24 kbar to 25 kbar. This increase in T and the slight
461 increase of P along the prograde path is confirmed by the spatial distribution of the
462 obtained T and P when plotted on a map: omphacite grains show high P at ~ 25 kbar,
463 and are zoned in T from 650°C in the old grain cores to 750°C in the old grain rims.
464 Clinopyroxene in the symplectite shows a different trend with a decrease of both P
465 and T with the decreasing size of the intergrowths (Fig. 9). This interpretation on the
466 preservation of P and T in symplectite during the exhumation is in good agreement
467 with the reported high cooling rates (Guillot et al., 2009). This example typifies the
468 importance of the mapping approach, which allows to test for relationships between
469 P - T conditions and the textural information from metamorphic microstructures.

470

471 **4. Concluding remarks**

472 This paper describes XMapTools, a MATLAB©-based GUI program to quantify raw
473 X-ray electron microprobe data using internal standards, plot chemical diagrams and
474 calculate P - T conditions of crystallization for metamorphic parageneses. The
475 XMapTools program includes 15 user-friendly main functions for the different steps

476 to the procedure, from the loading of the raw data to calculating P - T maps, and two
477 external modules *Chem2D* and *TriPlot3D* with independent graphical user interfaces
478 to plot chemical diagrams. Beside the treatment of compositional maps, XMapTools
479 offers the possibility of estimating thermobarometric conditions, which can be linked
480 to the observed deformation features. For the study of metamorphic and magmatic
481 rocks, a set of external functions specific to geothermobarometry is also included.
482 This set comprises a range of structural formulae functions for usual rock-forming
483 silicate minerals as well as empirical and semi-empirical geothermobarometers from
484 the literature. Application of XMapTools to an eclogite sample shows that the
485 accuracy of the mapped minerals composition is good enough to discuss the
486 compositional-structural- P - T relationships based from Na distribution in
487 clinopyroxene. A strong link between metamorphic textures and composition has
488 been found, and the retrieved P - T information gives a detailed reconstruction of the
489 metamorphic history of the sample.

490 A more detailed thermobarometric study can be made using independent programs
491 such as e.g. Theriak-Domino (de Capitani and Petrakakis 2010) or Tweep (Berman,
492 2007) with the whole range of mineral compositions derived from XMapTools, which
493 can be easily exported to the required formats. Moreover, an interesting feature of
494 XMapTools is the possibility to calculating local bulk rock compositions from
495 selected parts of the 2D maps. Such compositions can be used to calculate the stable
496 mineral assemblages, compositions and abundance by free energy minimizing (e.g.
497 Powell, 2008), and to compare them with the observed features. This approach,
498 illustrated in Lanari et al. (2013) for the example discussed in the present
499 contribution, can provide valuable information on the degree of achievement of
500 thermodynamic equilibrium, the link between deformation and reequilibration, and

501 possibly the extend of mass transfer controlled by deformation. Future release of
502 XMapTools will incorporate energy minimizing and multi-equilibrium modules to
503 facilitate advanced thermobarometric studies.

504

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513

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731 **Figure Caption**

732

733 **Fig. 1:** *XMapTools* v1.5.2 graphic user interface. The displayed image is the raw Al-
734 content map of the sample 'Eclogite' (see text for details) unit: number of recorded
735 counts.

736 **Fig. 2:** *XMapTools* operating diagram, schematizing the structure of the program. All
737 steps marked with a star require user action. Light arrows indicate the way forward,
738 bold-arrows the transition between the different sub-programs (Xray, Quanti, Results,
739 see text), and the dashed arrows the available feedback.

740 **Fig. 3:** Intensity recorded on the map versus oxide weight percent concentrations for
741 Si in the studied sample. Blue crosses show point analyses, lines are regressed
742 calibration curves obtained using the median approach described in text. The
743 precision is given depending on the intensity (% at 2σ) following equation 1 (see
744 text).

745 **Fig. 4:** Results from the *XMapTools Chem2D* module. (A) The clinopyroxene
746 compositions are plotted in a binary diagram Na vs Mg. Unit is per formula unit
747 (p.f.u.). The pixels displayed in the map are colored in red. (B) Density map
748 calculated from the binary diagram (see text for details). (C) Map of the analyzed area
749 in which clinopyroxene pixels selected in A are in red and the unselected pixels in
750 blue. Black pixels do not belong to the clinopyroxene mask. Selected Na-rich pixels
751 correspond to 25% of the total clinopyroxene pixels.

752 **Fig. 5:** Results from the *XMapTools TriPlot3D* module. (A) Clinopyroxene
753 compositions plotted in a ternary diagram jadeite-diopside-hedenbergite. Unit is the
754 end-member proportion. The selected pixel groups displayed into a map in C are
755 colored according to their group (blue: group 1, cyan: group 2, yellow: group 3). (B)

756 Density map calculated from the ternary diagram. (C) Map of the analyzed area, in
757 which the selected groups of clinopyroxene pixels in A are plotted with the same
758 colors as in A.

759 **Fig. 6:** Phase masks for the “eclogite” sample (A) computed using the ‘normalized’
760 method (see text). The part used to compare the two available methods is marked
761 using a dashed rectangle. (B) Comparison between the “classical” and “normalized”
762 methods with a difference image in which black pixels are the pixels not allocated to
763 the same groups with both methods.

764 **Fig. 7:** Na-content of clinopyroxene (including omphacite). The different stages of
765 crystallization (labeled 1 to 4) are discussed in the text.

766 **Fig. 8:** Diagrams showing the difference between point analyses composition
767 (standard) and the standardized composition on the same location on the X-ray maps
768 for garnet and different elements. (A) SiO₂, (B) Al₂O₃, (C) FeO, (D) CaO, (E) MgO,
769 (F) MnO, (G) TiO₂, (H) K₂O, (I) Na₂O. *BDL*: below detection limit.

770 **Fig. 9:** P-T path and P-T maps of the Stak sample estimated from the compositions of
771 clinopyroxenes (see text for details). The interpreted *P-T* path is from Lanari et al.
772 (2013).

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775 **Table captions**

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777 **Table 1:** List of solid-solution models and associated end-members included in
778 XMapTools.

779 **Table 2:** List of exchange reaction calibrations included in XMapTools.

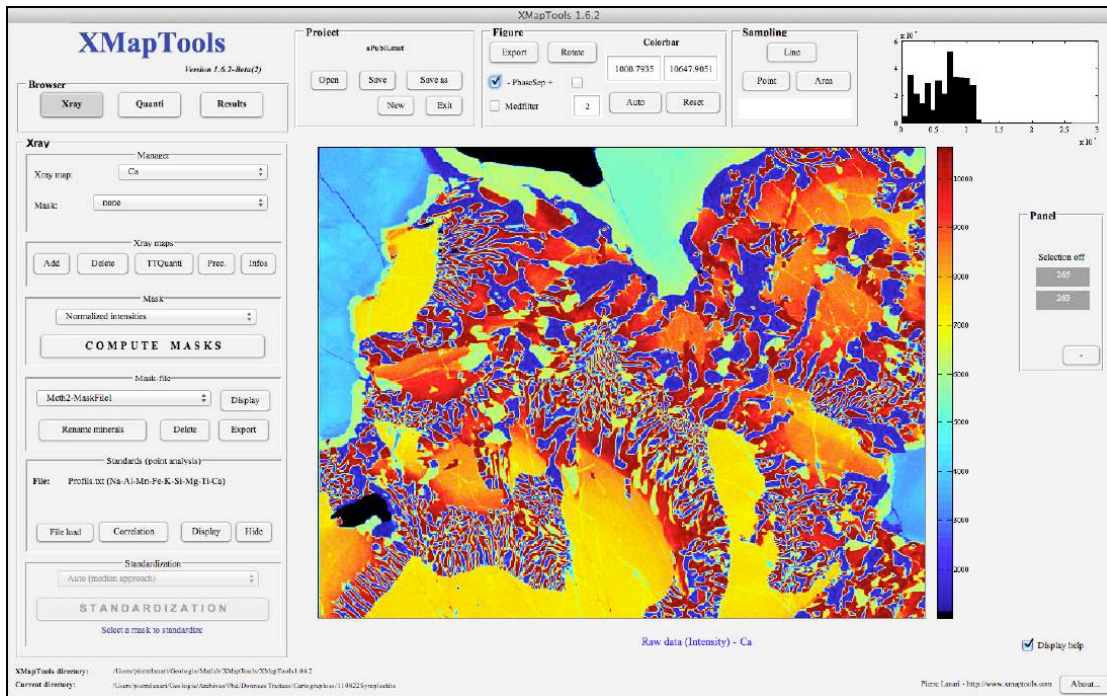
780 **Table 3:** List of empirical thermometers, barometers and multi-equilibrium functions
781 implemented in XMapTools.

782 **Table 4:** Phase proportions (volume %) estimated with XMapTools using the
783 available methods ‘normalized’ and ‘classical’. The difference in percentage is an
784 absolute difference.

785 **Table 5:** Uncertainties resulting from microprobe acquisition on raw data and error-
786 propagation using Monte-Carlo techniques on quantified data and structural formulae
787 for clinopyroxene. The precision at 2σ -level on raw data (in %) was estimated using
788 the equation 2 (see text) on the average intensity of all the pixels of clinopyroxene.
789 This uncertainty was propagated on the quantification process using a Monte-Carlo
790 simulation with $n=100\ 000$ analyses. The uncertainty was similarly propagated on the
791 structural formulae calculation process, including atom-site distribution.

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Figure 1

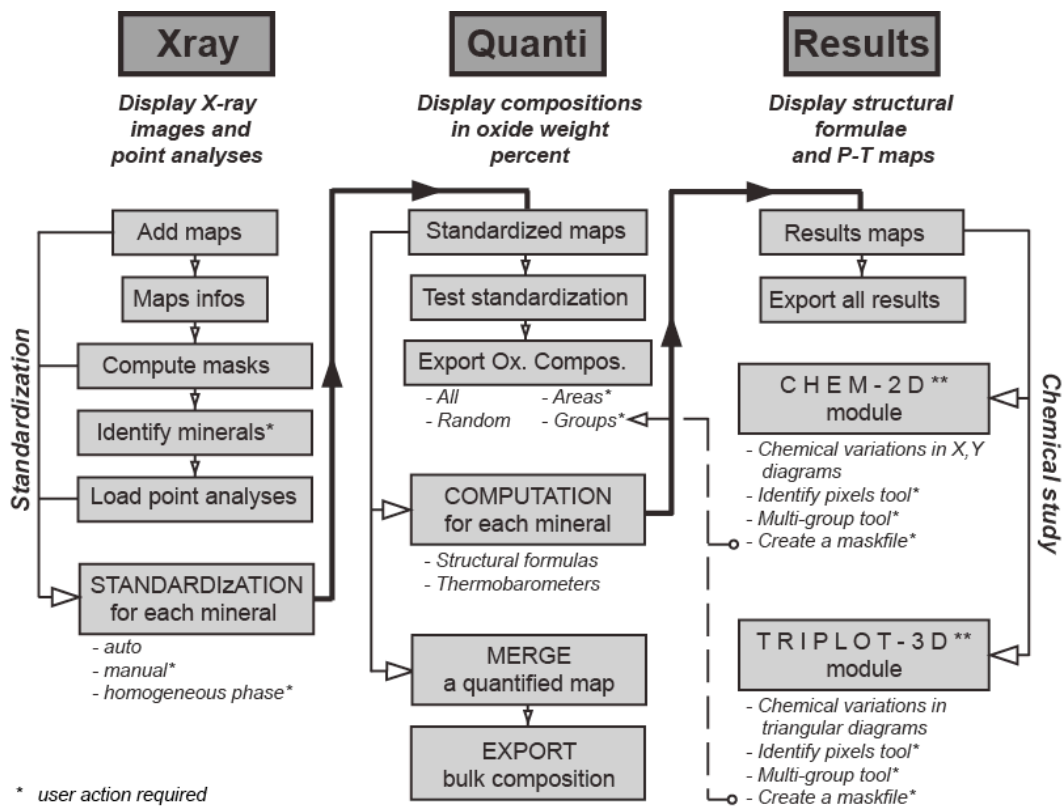


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Figure 2

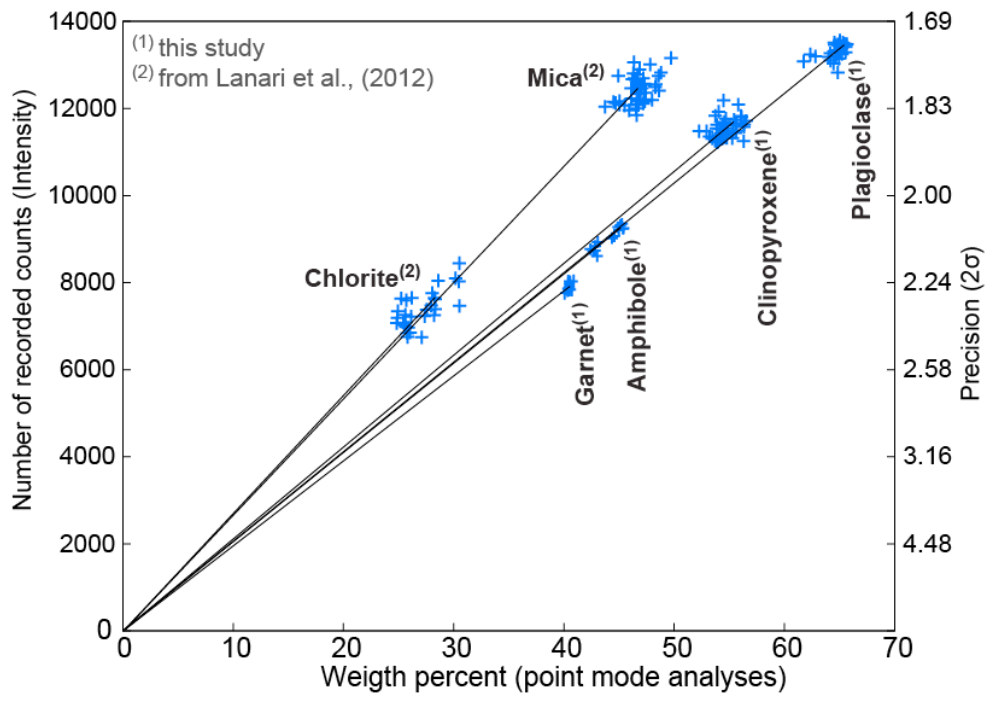


* user action required
 ** external GUI modules

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Figure 3



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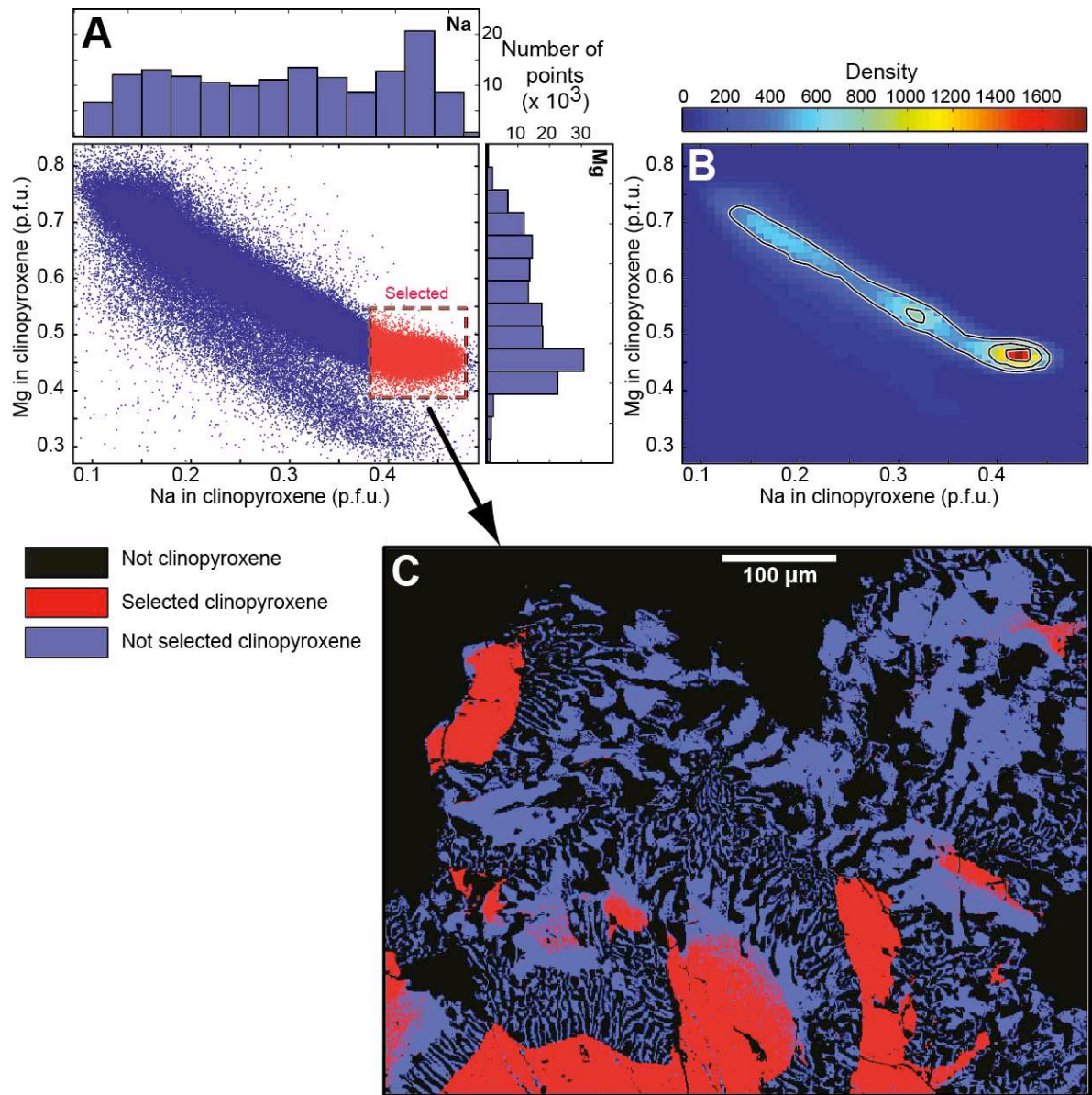
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Figure 4

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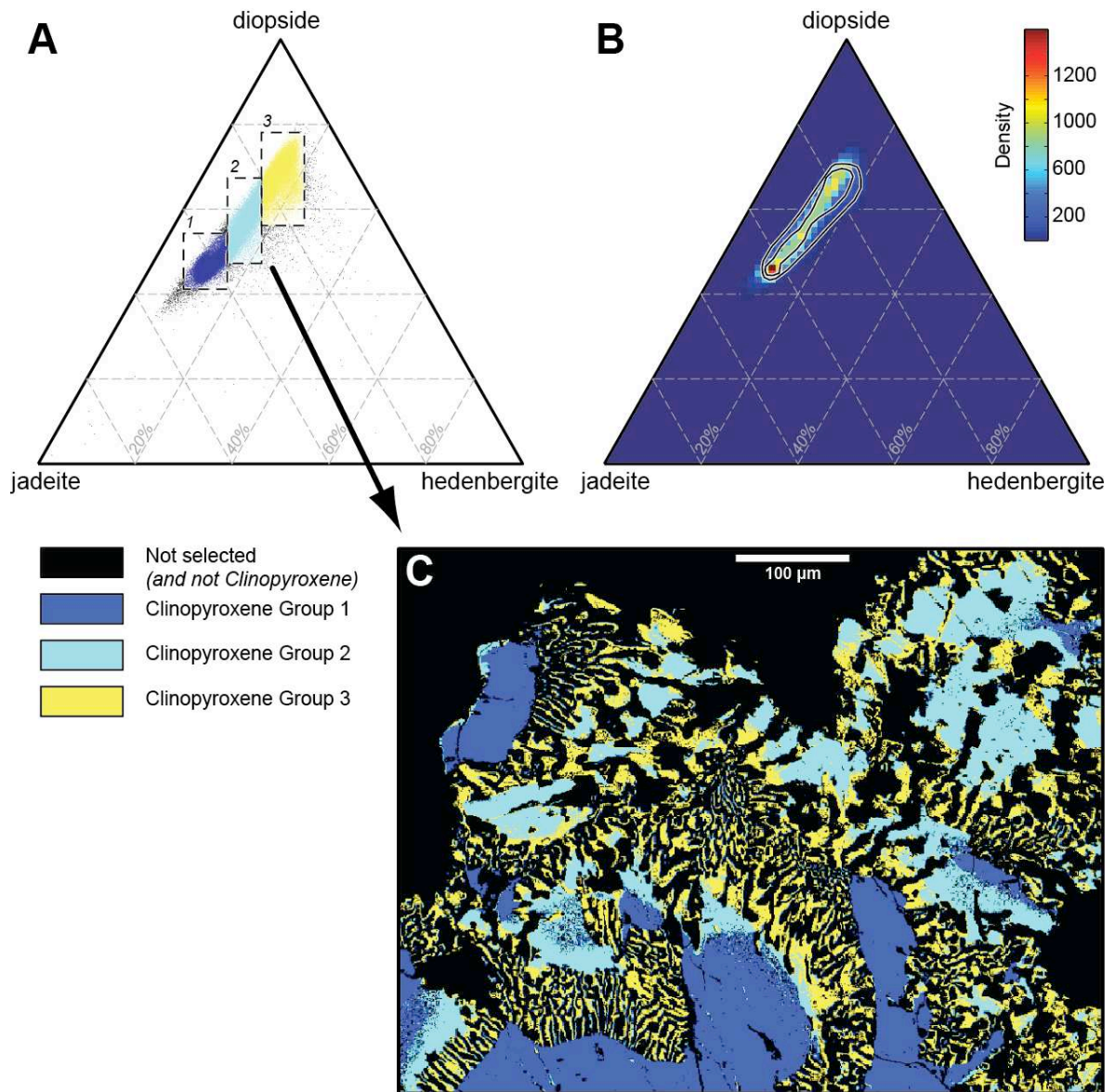
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Figure 5

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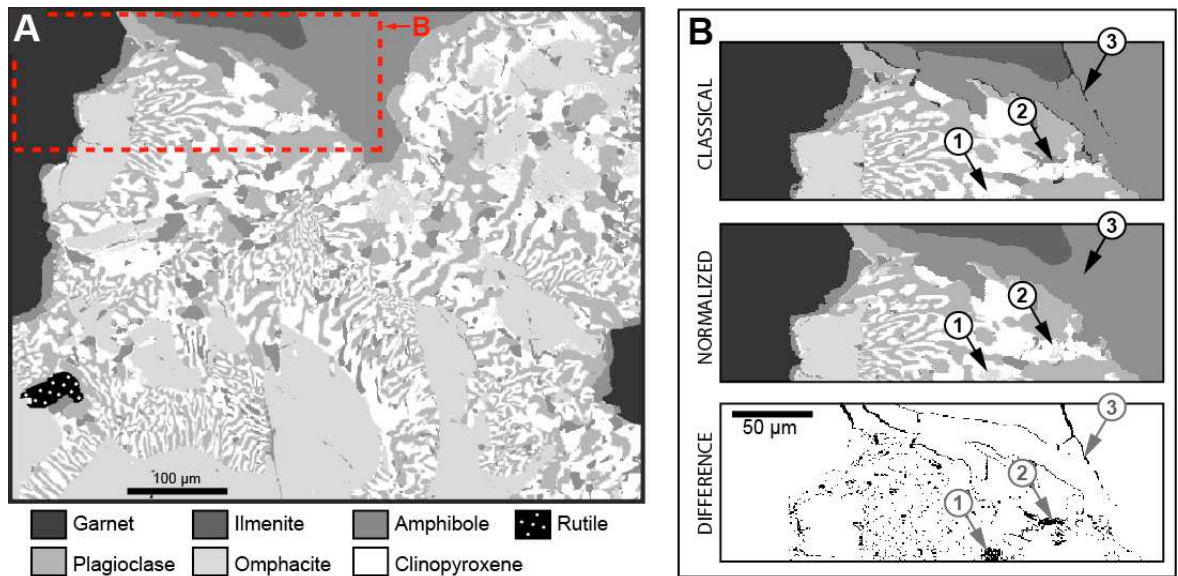
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Figure 6

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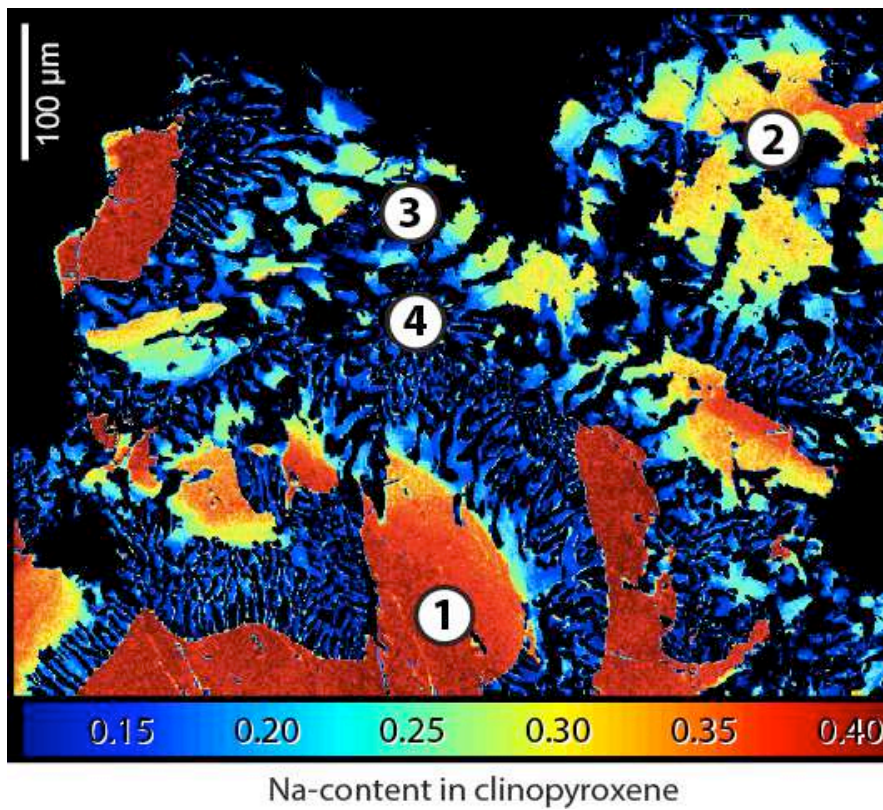
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Figure 7



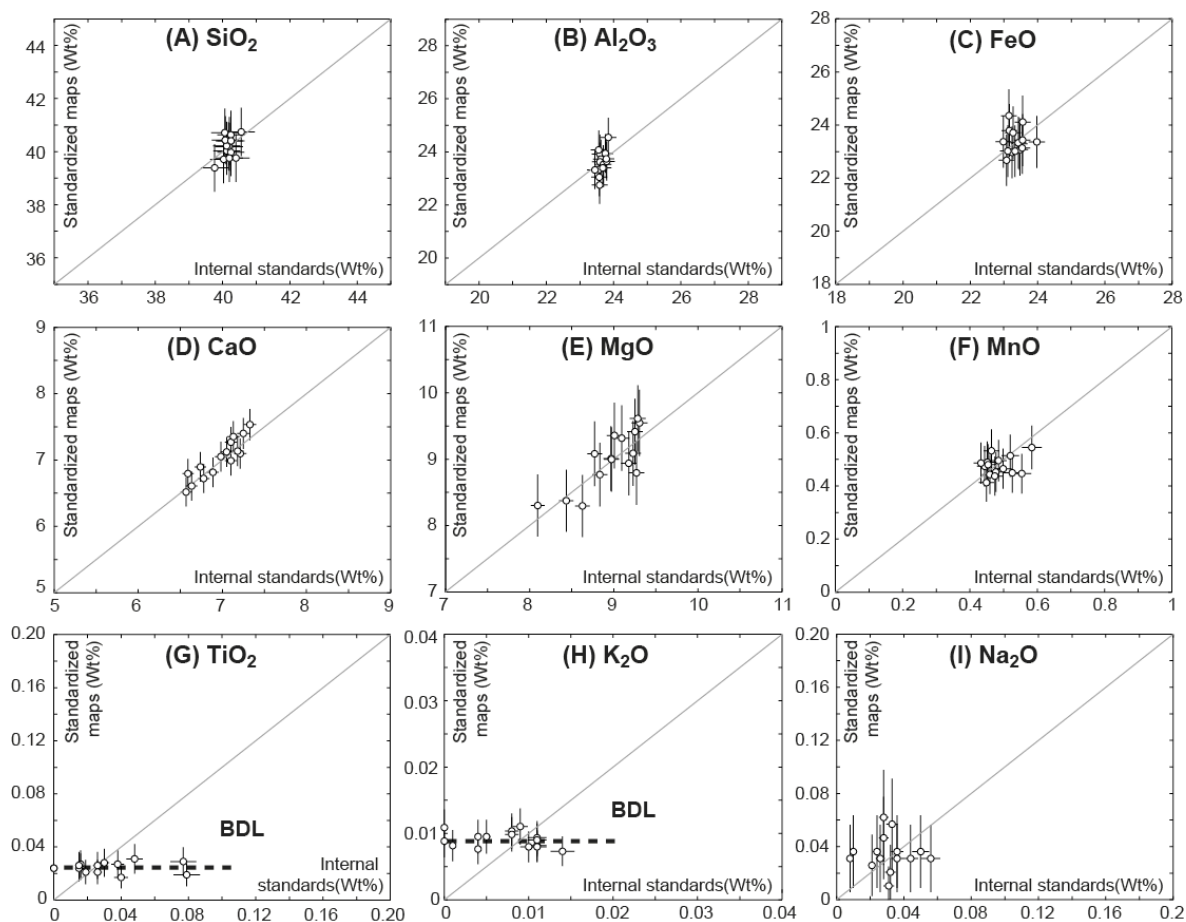
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Figure 8

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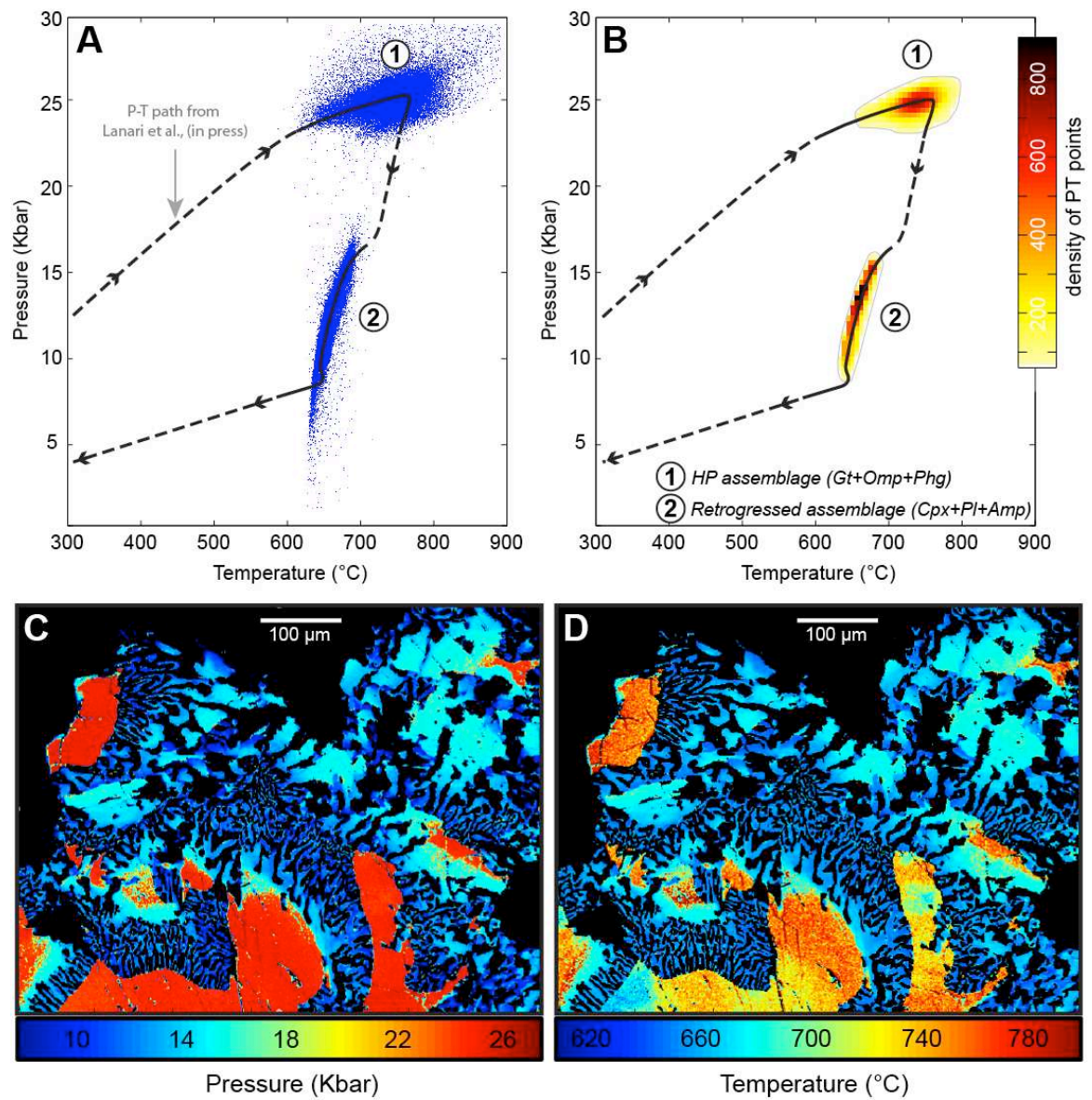
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Figure 9

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Table 1

Group	Mineral (*)	End-members (**)	References
Chain silicates	Amphibole (23)	<i>glaucophane (gl)</i> <i>tremolite (tr)</i> <i>f-tremolite (ftr)</i> <i>tschermakite (ts)</i> <i>pargasite (parg)</i> <i>cummingtonite (cum)</i> <i>ferri-tschermakite (mfets)</i>	Holland & Blundy, 1994; Dale et al. (2000, 2005); Spear (1995)
	Clinopyroxene (6)	<i>jadeite (jd)</i> <i>diopside (di)</i> <i>hedenbergite (hed)</i> <i>Ca-tschermak (cats)</i> <i>Acmite (acm)</i>	Spear (1995); Warren and Waters (2006)
	Orthopyroxene (6)	<i>Enstatite (en)</i> <i>Ferrosilite (fs)</i> <i>Mg-Tschermak (mgts)</i>	Holland and Powell (1998)
	Chloritoid (6)	<i>Fe-chloritoid (fctd)</i> <i>Mg-chloritoid (mctd)</i> <i>Mn-chloritoid (mnctd)</i>	Vidal et al. (1999)
	Staurolite (48)	<i>Fe-staurolite (fst)</i> <i>Mg-staurolite (mst)</i> <i>Mn-staurolite (mnst)</i>	Holland and Powell, (1998)
	Epidote (12.5)	<i>zoizite (zo)</i> <i>epidote (ep)</i> <i>Fe-epidote (fep)</i>	Holland and Powell, (1998)
	Cordierite (18)	<i>cordierite (crd)</i> <i>Fe-cordierite (fcrd)</i> <i>Mn-cordierite (mncrd)</i>	Holland and Powell, (1998)
Ortho- & ring silicates	Garnet (12)	<i>almandine (alm)</i> <i>pyrope (pyr)</i> <i>spessartine (spe)</i> <i>grossular (gro)</i>	Spear (1995)
	Olivine (4)	<i>forsterite</i> <i>fayalite</i>	Spear (1995)
Phyllosilicates	Chlorite (14)	<i>amesite (ames)</i> <i>f-amesite (fames)</i> <i>daphnite (daph)</i> <i>sudoite (sud)</i> <i>chlorite-Mg (afchl)</i> <i>chlorite-Fe (fafchl)</i>	Holland et al. (1998); Vidal et al. (2001, 2005, 2006)
	Micas (11)	<i>celadonite (cel)</i> <i>f-celadonite (fcel)</i> <i>muscovite (mus)</i> <i>paragonite (par)</i> <i>margarite (marg)</i> <i>phlogopite (phl)</i> <i>f-phlogopite (fphl)</i> <i>pyrophyllite (prl)</i>	Coggon and Holland (2002); Parra et al. (2002); Dubacq et al. (2010)
Framework silicates	Feldspar (8)	<i>albite (ab)</i> <i>anortite (an)</i> <i>microcline (mic)</i>	Spear (1995)

828 * Oxygen basis; ** abbreviation

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Table 2

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Method	Calibrations
Amphibole-Plagioclase	Blundy and Holland (1990); Holland and Blundy (1994)
Chlorite-Chloritoid	Vidal et al. (1999)
Garnet-Biotite	Thompson (1976); Goldman and Albee (1977); Holdaway and Lee (1977)
Garnet-Muscovite	Green and Hellman (1982); Krogh and Råheim (1978)
Garnet-Chlorite	Dickenson and Hewitt (1986); Grambling (1990)
Garnet-Amphibole	Ravna (2000b); Perchuk et al. (1985); Graham and Powell (1984)
Garnet-Cpx	Ravna (2000a); Ai (1994); Sengupta et al. (1989); Pattison and Newton (1989); Krogh (1988); Powell (1985); Dahl (1980); Ganguly (1979); Ellis and Green (1979); Mori and Green (1978); Råheim and Green (1974); Mysen and Heier (1972)

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Table 3

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Mineral	Thermometers	Barometers	Multi-equilibrium
Amphibole	T; Holland and Blundy (1994)	P; Anderson and Smith (1995) P; Schmidt (1992) P; Johnson and Rutherford (1989) P _{min} ; Johnson and Rutherford (1989) P _{max} ; Johnson and Rutherford (1989) P; Hollister et al. (1987) P; Hammarstrom and Zen (1986)	Amphibole + plagioclase* P from Schmidt (1992) and T from Holland and Blundy (1994). Amphibole + plagioclase* + quartz* P from Schmidt (1992) and T from Holland and Blundy (1994).
Chlorite	T; Inoue et al. (2009) T; Zang and Fyfe (1995) T; Jowett (1991) T; Hillier and Velde (1991) T; Cathelineau (1988) T; Kranidiotis and MacClean (1987) T; Cathelineau and Nieva (1985)		
Clinopyroxene		P; Waters (2002, 2003)	Cpx + garnet* + phengite* P from garnet – omphacite – phengites barometer of Waters and Martin (1993) and Waters (1996) and T from garnet – omphacite thermometer of Ravna (2000a) or Ellis and Green (1979). Cpx + amphibole* + plagioclase* T from amphibole – plagioclase thermometer of Holland and Blundy (1994) and P for the cpx – plagioclase barometer of Waters, (2002, 2003)
K-White mica		P; Massone and Schreyer (1987)	
Garnet	T; Creighton (2009) T; Kawasaki and Motoyoshi, (2011)		
Rutile	T; Zack et al. (2004)		

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* Fixed composition

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Table 4

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	Normalized	Classical	Difference (%)
Ti-oxide	0.43	0.43	0
Garnet	7.00	7.70	9.09
Fe-Oxide	1.10	1.13	2.65
Amphibole	13.20	12.77	3.37
Plagioclase	21.26	21.52	1.21
Omphacite	30.97	29.88	3.65
Cpx	26.04	26.57	1.99

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Table 5

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Raw data			Quantified data		
Element	Mean Intensity	Precision (% at 2σ)	Oxide	Composition	Error (2σ)
Si	11086	0.950	SiO ₂	54.718	0.528
Ti	93	10.35	TiO ₂	0.180	0.018
Al	2529	1.988	Al ₂ O ₃	9.690	0.194
Fe	631	3.981	FeO	4.529	0.176
Mg	1381	2.689	MgO	10.211	0.276
Ca	6486	1.242	CaO	16.379	0.206
Na	470	4.609	Na ₂ O	4.050	0.188
K	127	8.889	K ₂ O	0.020	0.002
			Structural formula		
				Composition	Error (2σ)
			Si_T1	1.962	0.010
			Al_T1	0.038	0.010
			Al_M1	0.371	0.010
			Mg_M1	0.546	0.014
			Fe_M1	0.136	0.005
			Ca_M2	0.629	0.008
			Na_M2	0.281	0.013
			XMg	0.801	0.008
			XFe	0.199	0.008
			Xjd	0.281	0.013
			Xdi	0.546	0.014
			Xhed	0.136	0.005
			Xcats	0.019	0.005

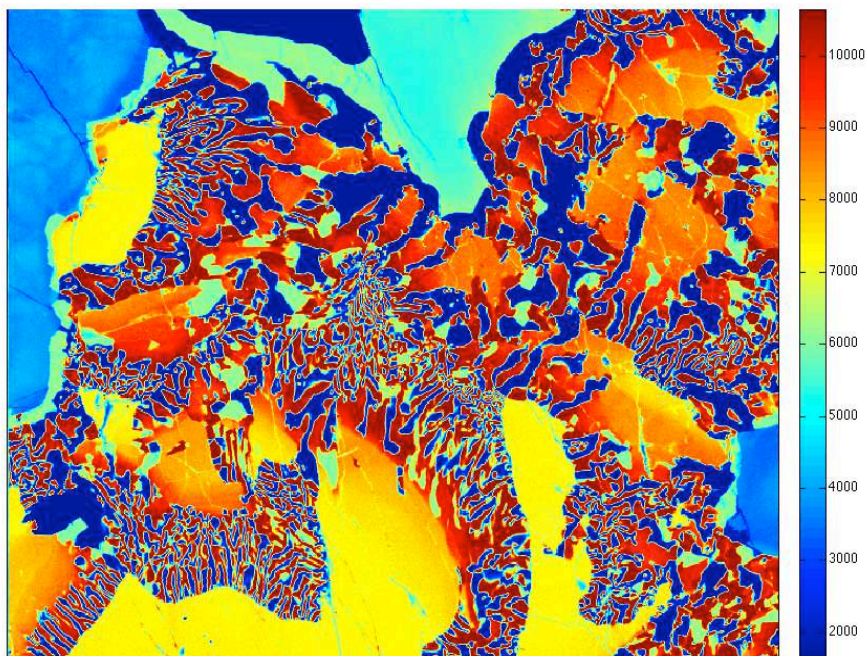
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851 **Appendix 1**

852 Ca.txt (file)



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854 *Ca.txt chemical image for the high-pressure Himalayan eclogite sample from the Stak*
855 *massif in northern Pakistan displayed using XMapTools (unit number of recorded*
856 *counts, auto-contrast).*

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