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# Chapter

# Spatial Visualization of Geochemical Data: Application to the Chichinautzin Volcanic Field, Mexico

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#### **Abstract**

The presence of spatial magma heterogeneities in volcanic monogenetic fields is a major observation discussed as well synthesized for worldwide volcanic fields. Magma heterogeneities still have not been visualized in the form of detailed spatial analyst tools, which could further help structuring works of geological mapping, volcanic hazard, and geoheritage evaluations. Here we synthetized 32 published datasets with a novel geochemical mapping model inspired by sub-disciplines of geomatic in one of the most documented monogenetic fields on earth: the Chichinautzin Volcanic Field (CVF) in Mexico. The volcanic units from CVF are covering the 2500 km<sup>2</sup> area, and its neighbor stratovolcanoes are bordering the limit of most volcanic centers (Popocatepetl, Iztaccihuatl, and Nevado de Toluca). The results illustrate polygons and point map symbols from geochemical markers such as Alkalis vs SiO<sub>2</sub>, Sr/Y, and Ba/Nb. The geochemical heterogeneity of the CVF monogenetic bodies decreases as it approaches the Popocatepetl-Iztaccihuatl stratovolcanoes. This alignment is not observed in the occidental CVF portion near the flank of Nevado de Toluca, but geochemical anomalies associated to markers of continental crust interaction such as Sr/Y follow elongated patterns that are not strictly following structural lines and faults mapped on surface.

**Keywords:** monogenetic, spatial interpolation, trans-Mexican Volcanic Belt, geochemistry, Chichinautzin

#### 1. Introduction

The presence of volcanic centers clustered in a monogenetic field involves possible control from the feeding plumbing system architecture. The range of chemical composition (i.e. major elements abundances such as  $SiO_2$  contents, trace elements, etc.) from the effusive as explosive volcanic rocks also lead to various interrogations regarding origin of the magma that circulate in the lithosphere below monogenetic volcanic fields. Most of all, the presence of spatial magma heterogeneities is a major observation discussed and synthesized for volcanic fields in subduction zones [1–3]. Visualization tools are required to facilitate these observations and analyses for understanding the building of minor volcanic centers as defining the origin of the magma in monogenetic fields.

The Chichinautzin Volcanic Field (CVF) in the center of the Trans-Mexican Volcanic Belt (TMVB) represents the ideal study case to improve observations and simplify visualization of spatial heterogeneities among a volcanic field. The high sampling density of volcanic rock samples in CVF literally favor the area for such studies. Building a spatial visualization model becomes necessary regarding natural hazards because of CVF vicinity to the greater Mexico city, globally one of the most populated urban area.

A novel spatial model and geomatic tool are thus presented here to illustrate the geochemical dispersion from sampled volcanic rocks. This spatial model is simple and involves high precision for object localization on a map. Geochemical markers (geomarkers) related to classic igneous petrological analyst tools now are given quantitative symbols and projected on a digital elevation model (DEM) background. Point symbols and polygons that mark specific ranges of values from the geomarkers show clear spatial magma heterogeneities that can be interpreted and used in various disciplines of geosciences.

#### 1.1 Chichinautzin volcanic field

The Chichinautzin Volcanic Field (CVF) in the center of the Trans-Mexican Volcanic Belt (TMVB) is a key zone to understand recent monogenetic magmatism in a subduction zone. The volcanism of CVF and seismic activity underneath is rift-related and is also affected by the subduction of the Cocos plate under North American plate [4–9]. The age of volcanism is relatively young; geochronological 14C data, paleomagnetic measurements and the <sup>40</sup>Ar/<sup>39</sup>Ar method applied on volcanic rocks give ages that goes up to 1200 ka [10–12]. The youngest eruption is the Xitle scoria cone around 1665±35 years b.p., whose lavas destroyed and buried the pre-Hispanic settlement of Cuicuilco [13].

The question of where volcanism occur is particularly of interest for geologists since around the populated valley of the greater city of Mexico, the CVF includes more than 220 quaternary cinder cones and few shield volcanoes, with their associated lava flows and tephra sequences (**Figure 1a, b**). In addition, the region is still "geologically active"; the volcanic structures tend to be aligned on E-W normal faults [14] with stratovolcanoes (Popocatépetl-Iztaccihuatl and Toluca) occurring at the intersection of N-S and E-W faults [16, 18]. The source of magmatic and seismic activity is also of concern [19], beneath all CVF, the inferred depth of the slab interface is changing between 80 km and drastically to levels far deeper than 100 km [8, 20]. The crustal thickness beneath the CVF is ~40 to 50 km which is the greatest in the TMVB [8, 9].

Noteworthy in the field of geochemistry, [14] mentioned a spatial variation from the composition of volcanic rocks and schematic sections were proposed to show where are the different kind of magmas in CVF [15, 21]. Overall, there have been lots of work done in the CVF relating its heterogeneity, and with the rapid development of analytical techniques in geochemistry, a new data compilation was needed after [22].

The geochemistry of the volcanic products in the CVF is characterized by basaltic andesite to dacitic rocks with alkaline to calc-alkaline affinities [9, 23]. The majority are subalkaline, except for the most mafic samples (ex: Chichinautzin and Guespalapa) which are transitional and plot in the alkaline field [14]. Mafic melt compositions (basalt, basaltic andesites) are found in olivine phenocrysts holding glass inclusions of ~49 to <54 wt.% SiO<sub>2</sub> (i.e. see Xitle, [24] and Pelagatos, [25]).

Since the first proposed petrogenetic explanation from Gunn and Mooser works (1970s), the origin of magmas heterogeneities in the CVF is still debated. Two different types of mantle-derived primitive mafic magmas have been suggested for

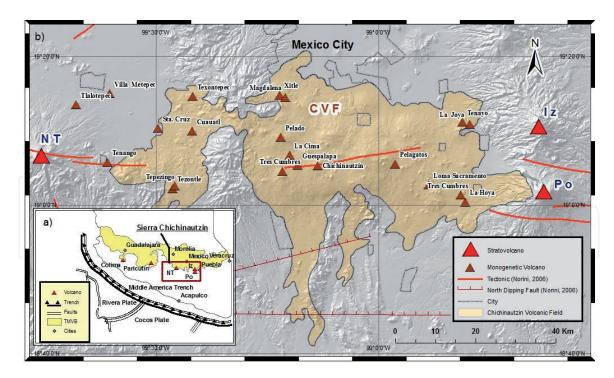


Figure 1.

Area of study (map modified from the following authors; [13–15]) including the Chichinautzin volcanic field (CVF) (shaded polygon), well known monogenetic volcanic centers (small solid triangles), stratovolcanoes (big solid triangles), the urban areas (gray limits), and tectonic features from [16] (large lines). A digital elevation model (DEM) was built to represent the topography with a 30 meter-resolution. The digital elevation model (DEM) was built in ArcGIS to represent the topography with 30 meters resolution (access from INEGI, [17]). The smaller map represents the tectonic context of the trans-Mexican volcanic fault (TMVB) and Chichinautzin volcanic field (CVF) emplacement (map modified from [14, 15]. The geological and geophysical features of the TMVB (shaded area), active volcanic centers (solid triangles), and major cities (full circles) and the CVF (shaded rectangle). Part labels "CVF" is for Chichinautzin Volcanic Field, "NT" is for Nevado de Toluca, "Po" is for Popocatepetl and "Iz" is for Iztaccihuatl.

CVF based on Sr-Nd isotopes, trace elements and mineralogical features [15, 26]. The first type is an OIB-like mafic magma, and is characterized as anhydrous [6, 9, 15, 23, 27–29]. The second type is associated to a metasomatized mantle source, with incompatible elements of a depleted mantle source, but enriched in mobile elements that are possibly coming from the subducting slab [6, 9, 23, 29].

#### 1.2 Method

A database of whole rock composition was produced by the compilation of geochemical data from 583 samples of volcanic materials within the CVF (Appendices). A total of 32 references was used containing whole rock data (major and trace elements from (A) Scoria cones in the Chichinautzin Volcanic Field (sample of lava, bomb and scoria), (B) Iztaccihuatl, (C) Popocatepetl, (D) Nevado de Toluca. In the case of stratovolcanoes (B-C-D), only were considered juvenile samples of pyroclast, pumice or a dome fragment.

#### 1.2.1 Geomarkers defined

Pairs of geochemical elements from whole rock analysis and representing high density sampling area were chosen based on their petrogenetic significance. All referenced data from the geochemical dataset of CVF were given latitude and longitude coordinates (Appendices I, II), then a spatial attribute is automatically associated when the tables are uploaded in a Geographic Information System (GIS). This database was projected with ArcGIS software [30] to detect any spatial trend.

The compiled data come from 32 published works between 1948 and 2011 (See Appendix II for a list of the references used). Also, for comparison, data from the neighbor polygenetic volcanoes are included: Popocatepetl, Iztaccihuatl and Nevado de Toluca.

The systematic approach described above was possible to propose with a recompilation and a methodical statistical investigation of geochemical tracers of petrogenetic and tectonic processes. The statistic distribution of a single ratio is called a geochemical marker (geomarker).

In this review, 2 geomarkers were chosen based on the significance they represent in rock classification and petrogenesis. Two datasets of each geomarker were then created from the central geodatabase and plotted in the GIS map:

- 1. The alkali geomarker (464 datas) which represents the alkalinity of the rocks and may be indicative of assimilation from continental crust during formation of the magmas. The ratio is obtained by dividing alkalis over silica which transform the conventional bivariant graphic into a univariable value for mapping [31–33]. The Sr/Y geomarker (228 datas) is used to evaluate the significance of the alkali geomarker. The alkalinity of the rocks has high probability to be associated to the systematic of crustal thickness when high values from Sr/Y point symbols match areas with strong alkalinity. Th Updates in Volcanology Transdisciplinary Nature of Volcano Science e equilibrium of plagioclase fractionating on Sr and both amphibole + garnet phases on Y is recognized to correlate with the variation of crust thickness in arc magmas [27].
- 2. The Ba/Nb geomarker (320 data) is used to geochemically characterize the tectonic environment. Ba is more soluble and mobile in subduction fluids [34]. Nb is considered immobile in subduction fluids, it is not added to the mantle asthenospheric wedge and the rising basaltic melts, because it remains in the metamorphic rocks of the subduction zone [35, 36]. High ratios of Ba/Nb are then suspected of magmas enriched in fluid coming from subduction.

#### 1.2.2 Geostatistics to support spatial model

The method proposed in this work uses spatial interpolation models which require evaluation depending on the data dispersion of the samples and previous geostatistics made on the databases. The principle of interpolation in cartography is applied to improve visualization of regional patterns of a natural phenomenon and to generalize a numerical distribution in a certain region [37, 38]. The equations of such models can be consulted in [37, 38], and also searched in the GIS tutorials [30, 39].

Evaluations on previous interpolation approaches to CVF were resumed in [40]. Intercomparing of kriging, inverse distance weight (IDW) and Linear Decrease (LD) is necessary due to the difference of input parameters between each approach. Ordinary kriging is proposed here according to the high density of samples in several areas between Popocatepetl and Nevado de Toluca flanks, mostly between latitudes 19°00′ and 19°20′ (**Figure 1**). As petrologists are interested by geological factors that influence the geomarkers at different scales [27, 34–36], the semi-variogram evaluation preceding the ordinary kriging becomes necessary to determine at what distance are the geochemical changes tendencies [40]. As a matter of fact, the common analyze of nugget, sill, and range for determining the spatial dependence of geochemistry is unique to this interpolation technique [37, 38]. If the preferential orientation of data positions in the map was constrained (i.e. anisotropy), the angle (in degrees) could be manipulated by specific kriging methods in several pieces of GIS software. In CVF, as seen in **Figure 1**, the large 2500 km² area contains too many

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sources of anisotropy, which lead to eliminate angles dependence along the input parameters.

#### 1.2.3 Evaluation of the physical environment

The interpolation model is only applied for the monogenetic cones of the CVF, because the material dispersion is not the same for the eruption of stratovolcanoes. A map with punctual representation of each calculated average composition at each volcanic emission center is compared with the original dataset (**Figure 1**) and used for the interpolation model. When the raster model is obtained for the alkalis and Ba/Nb geomarkers, four categories of raster values are associated to quartiles in four categories of colors used for the geomarkers of CVF and then transformed into polygon shapefiles. The mapped results of interpolation of CVF is sliced in the GIS with the same four quartile limits (the same colors) for each range of values.

As for other interpolation techniques, the limiting distance (Do) chosen for considering a maximum number of points is important [37, 38]. This is determined for modeling the distribution of rock geochemistry because it is setting a maximum distance of influence between different sampled sites. This limiting distance (Do), or technically called "search radius" use a weighting exponent adjusted to the influence of the distance between sample points. First, to provide estimated values at locations of interest and second, to generate values presenting the same dispersion characteristics as the original data [38].

To determine Do, the physical environment must be considered. In this study, a Do of 6000 m was used based on the maximum length of lava flows measured from 76 cones in CVF, this is considering that effusive rocks are emitted at larger distance than ballistic projectiles from explosive eruptions. A 6000 m buffer area was thus drawn covering almost all the data on the map and tried to avoid isolated samples (sometimes outliers). The buffer separates the farthest sample on the map from this artificial boundary. The radius is especially useful for limiting the interpolation calculation. In addition, by clipping for the same distance the resulting matrix image, a better design of the geomarker dispersion model is obtained. The drawing of the four polygons color categories is recommended to fit exactly with the four quantile categories that represent the range of pixel values.

#### 1.2.4 Evaluation of spatial model

The datasets of alkalis and Ba/Nb are analyzed with spatial geostatistical tools, specifically the Moran's Index (I) because of its simple interpretation for determining the level of spatial autocorrelation (**Table 1**). The spatial autocorrelation from such index measures dependence among nearby values in a spatial distribution [41]. It considers that variables may be correlated because they are affected by similar processes, or phenomena, that extend over a larger region [38, 41]. The index is the result of a specialized algorithm; it first takes into account the classes of distances created for point pairs that are more or less at the same distance to each other [30, 39].

For all point pairs within a distance group, the spatial autocorrelation index (I) is calculated and it can be summarized as follow [equation in ILWIS 3.7, 38]: strong positive autocorrelation (I > 0), strong negative autocorrelation (I < 0), or random distribution of values (I = 0).

Pattern characteristics of the data were also analyzed. The parameter Prob1Pnt was calculated using ILWIS 3.7. This calculates the probability that within a certain distance (column distance) of any point, at least one other point will be found, i.e.

| Spatial autocorrelation | Alkalis | Ba/Nb |
|-------------------------|---------|-------|
| Moran's I index         | 0.42    | 0.48  |
| Z score                 | 2.81    | 3.02  |
| Dispersion              |         |       |
| Prob1Pnt (m)            | 8250    | 9500  |

Recall the legend for Moran I: Strong positive autocorrelation (I > 0), Strong negative autocorrelation (I < 0), Random distribution of values (I = 0).

#### Table 1.

Results of parameters from spatial autocorrelation (Moran Index, Z Score) and dispersion functions (Prob1Pnt).

the probability to find the nearest neighbor of any point list within this distance. It is a direct measure of dispersion and for the case of CVF, it indicates if the sampling area is well covered for the 220 identified volcanic centers (**Table 1**).

To evaluate "how good" is the model, cross validation calculation was used where the goal is to have the smallest root-mean-squared prediction errors [30, 38]. The cross-validation method is based on percent error or PE (%) and a RMSE (root mean square error). It is the mean of the squared difference between the observed value (Pi\*) and the predicted value (Pi), where n is the number of observations.

#### 1.3 Results

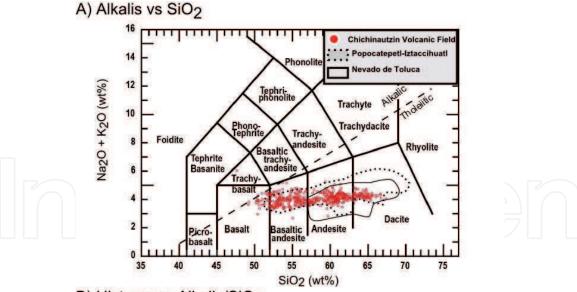
## 1.3.1 Alkali geomarker

The geochemistry diagram shows alkaline enrichment in the four groups and greater dispersion for CVF (**Figure 2A**). The alkalinity is stronger for the stratovolcanoes and the rock names vary from basaltic trachy andesite to trachydacite. The CVF is classified between basaltic andesite to dacite. Iztaccihuatl have similar values from sample of East CVF or Valley of Puebla (same trend). The Nevado de Toluca has strong alkalis values (third and fourth quartiles).

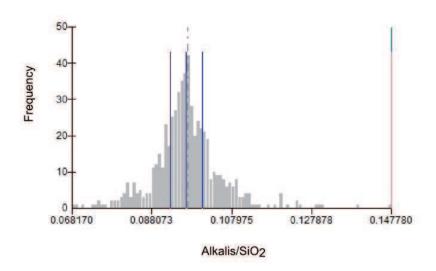
As seen in **Figure 2B**, the total sample distribution is almost a Gaussian curve for all incorporated samples in the database. The Moran Index (**Table 1**) demonstrates data that are spatially clustered, but the distribution is not random. The study gives a probability pattern to find a first interpolation point for 8250 m.

From the semi-variogram evaluation on the model (**Figure 2C**), the determined range (first plateau) is given with the spherical function model at 13,000 m which indicates a smaller scale influence compare to the other ratios. It is interesting to see a maximum over ~20,050 m and for other distances (plateau at 39,500 m) which indicates different scale influence of the alkalinity.

High values (third and fourth quartiles) from the alkali geomarker as spatial dispersion are variable at large scale in general, from east to west in CVF (**Figure 3**). Large surface of high alkalinity and high Sr/Y ratios are found near the Sierra de Las Cruces (SDLC) and Nevado de Toluca, some others south of Valley of Puebla Scoria Cones and in the center of CVF. Regionalization of low values is found for large area in the center of CVF, but some low Sr/Y ratios do not match with high alkaline contents for Guespalapa, Chichinautzin, Herradura and Suchioc samples. The distribution of alkalinity follows elongated polygons over CVF (NE-SW and SE-NW tendencies), but small anomalies are also observed. Stratovolcanoes are represented by high values of Sr/Y among point symbols, but geostatistics show large ranges of alkalinity.



B) Histogram: Alkalis/SiO2



# C) Semi-variogram: Alkalis/SiO2

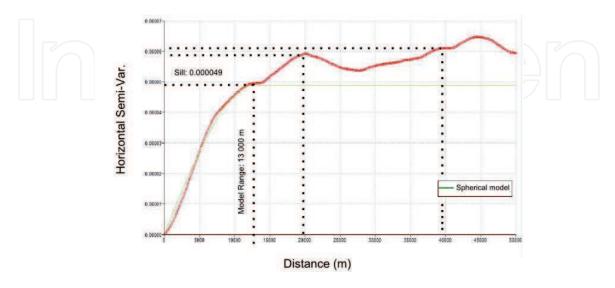
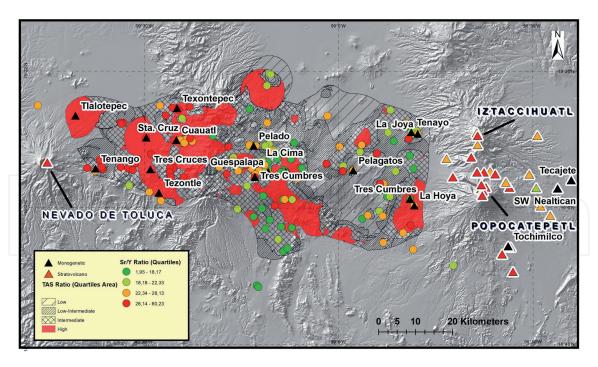


Figure 2.

(A) TAS diagram (alkali vs. silica) for all CVF data point. Data from Popocatepetl-Iztaccihuatl and Nevado de Toluca are also included for composition. (B) Distribution diagram of the alkali geomarker. The solid vertical lines are the four quantile limits (0.093, 0.097, 0.101, 0.148) with the second and fourth representing the median and the maximum and the dashed vertical line represents the average ( $\bar{x}$ =0.097). (C) Semi-variogram for the alkali geomarker for all CVF data points.



**Figure 3.**Symbol map and spatial overlay results of ordinary kriging for alkalinity ratio. The point map symbol overlays represent center of emission and volcanic deposits with their respective average alkalinity. The color legend is from Sr/Y ratio separated with quartiles. The circle point symbols represent monogenetic cones, and the triangle point symbols represent important deposits emitted by the stratovolcanoes. The symbol codes in the legend attributed for the ratio alkali categories in the legend are built with quartiles.

#### 1.3.2 Ba/Nb geomarker

The geochemistry diagram, while in most cases there is no correlation with the large variation of Nb datas, Ba values generally are higher for CVF, but there are no positive-negative relationships with Nb (**Figure 4A**). CVF have widely scattered values, the Nb values of Popocatepetl and Iztaccihuatl are generally lowers, but Nevado de Toluca's values are higher.

The total sample distribution appears as two Gaussian curves. Those curves represent two populations of data with distinct patterns and two central tendencies (**Figure 4B**). Since Ba is not variable inside each group, the distribution of the Ba/Nb ratio is controlled by Nb. From Moran Index, the data form clustered pattern without a random distribution. The study gives a probability pattern to find an interpolation point for 9500 m so the influence between each sample is less important than for alkalis. From the semi-variogram, the determined range is given at 14,500 m which indicates a larger scale influence compare to the other ratios. A maximum is present at ~38,000 m (**Figure 4C**).

On the map, there are important first order tendencies. The entire CVF is exceptionally low, but regionalized and high values are found around the stratovolcanoes where the Nb is the lowest (La Hoya, Loma Sacramento, Tenayo), but also through SDLC or near Nevado de Toluca. The geochemistry changes from east to west starting from the Popocatepetl area (**Figure 5**). The polygons from the Ba/Nb spatial model are clearly elongated in a N-S direction.

#### 1.4 Discussion

#### 1.4.1 The visualization technique

The analysis of pattern (**Table 1**) showed that samples were grouped in disordered cluster without random dispersion, reflecting the different field strategies

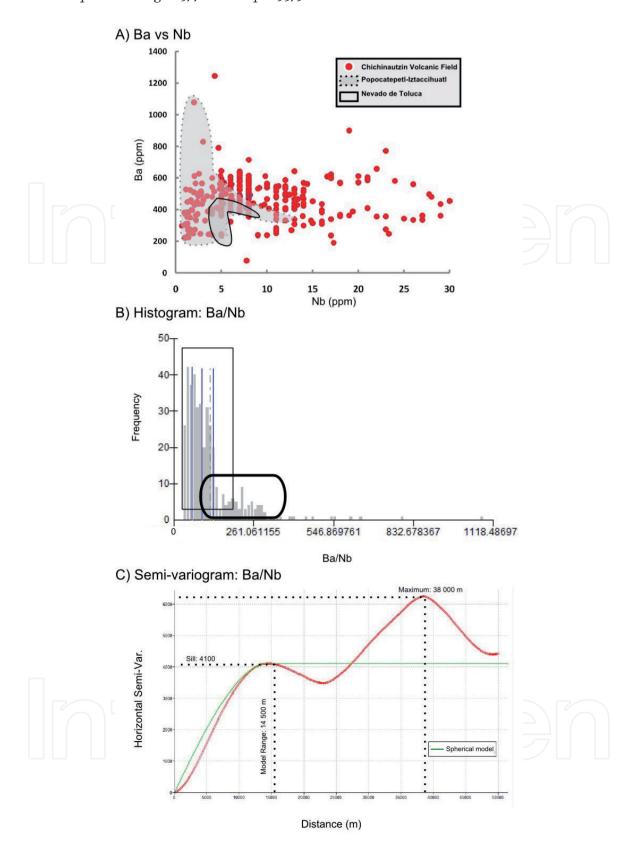


Figure 4.

(A) Ba vs. Nb diagram for all CVF data point. Data from Popocatepetl-Iztaccihuatl and Nevado de Toluca are also included for composition. (B) Distribution diagram of the Ba/Nb geomarker. The solid vertical lines are the four quartile limits (41.1, 74.0, 114.0, 1081.0) with the second representing the median, and the fourth quantile represents the maximum. The dashed vertical line represents the average ( $\bar{x}$ =104.9). Circular box represents where are the monogenetic cones in the population, and the thin border rectangular box represents the stratovolcanoes. (C) Semi-variogram for the Ba/Nb geomarker for all CVF data points.

that influence the targeted investigated area of CVF. This dispersion diverges from systematic grids performed for small scales mineral exploration tactics or soil surveys [38].

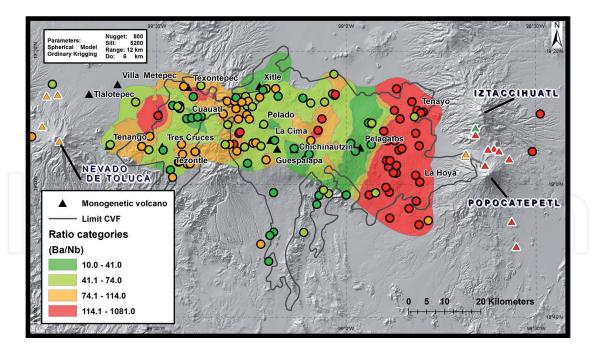


Figure 5. Symbol map and spatial overlay results of ordinary kriging for Ba/Nb ratio. The point map symbol overlays represent center of emission and volcanic deposits with their respective average Ba/Nb ratio. The circle point symbols represent monogenetic cones (n = 134), and the triangle point symbols represent important deposits emitted by the stratovolcanoes (n = 16). The color codes attributed for the ratio categories in the legend are the same for the point map symbol and surface layers.

The measure of dispersion gives values between 8250 and 12,900 meters and it is inversely proportional to the quantity of samples in each dataset. Despite those distances, the spatial dependence of the models varies between 13,000 and 18,000 meters (**Figure 2C**, **4C**; see semi-variogram evaluation). The changes of geochemistry are interpreted to occur for small distances between eruptive centers, but also for ranges over larger distances as it is shown for alkali, Sr/Y and Ba/Nb datasets. Finally, from observation of the point value symbol maps (Appendix I), despite of the rich geological knowledge and sampling works in CVF, the measure of dispersion allows to interpret an insufficient density of certain sampling area, particularly for monogenetic cones N-E of Xitle in urban sector, in the valley around Sta. Cruz volcano, and south of the CVF (forest).

The evaluation of rock chemistry affinity can be used to evaluate target for petrological investigation and resume spatial patterns as a clear idea of geochemical distribution of a monogenetic field. On the other hand, the presented methodology finds limitations for different reasons (we proposed four factors):

- 1. Detailed toponymic descriptions are furnished without coordinates of samples by some authors which complicate assigning geographical coordinates (Appendix II; the number of references being n = 15/32). This is in addition to the quantity of elements analyzed for geochemistry in certain sectors (different analytical instrument, necessity or not to use rare earth and trace elements) as the targeted material from the publication which involve for some authors to study different kinds of external and internal petrological processes.
- 2. Control of arbitrary parameters such as the search radius and weighting exponent in the interpolation approach can be affecting the error and precision of the model [40]. The IDW and LD techniques are ideal in areas without anisotropy and where the quantity of point neighbors is not critical (i.e. constant in a structured sample grid [30, 37–39].

- 3. Sampling density and dispersion as determined with (I) find limitations from the physical environment (topography, vent locations reported in literature, nonpreferential flow orientation, etc.).
- 4. Strategical sampling affects the distribution of sampling site positions (i.e. various objectives of petrological sampling, sample distance to road of access, uncertainties of rock sample association to emitting vent, etc.).

#### 1.4.2 Surface variation of the geochemistry

Trace element ratios Ba/Nb show first-order trends and one maximum in the semi-variograms for 38 km (**Figures 2, 4**). Spatial variations of trace element ratios are correlated for limits that correspond to larger distances. These changes of geochemistry are visible in a larger area and may be related to large-scale tectonic effects which may be associated to new input material from the subduction zone [3].

Alkalis shown on the maps has tendency of second order (for 13,000 m) and have different changes of spatial dependence for larger distances interpreted in the semi-variogram (**Figures 2,4**). These second plateau and maximum can also be interpreted as secondary large-scale tendencies. At local scale, it perfectly marks the regional heterogeneity known in the CVF, but larger scale effects also occur (i.e. For example Pelagatos and the center of the monogenetic field is clearly less evolved and less alkaline; see [25, 42, 43]).

The geochemistry of monogenetic cones satellites/boundaries of Popocatepetl, Iztaccihuatl: like the neighbor stratovolcanoes have volcanic arc affinity (high Ba/Nb), influence of crustal thickness (high Sr/Y) and constitute predominantly felsic rocks. Despite of this, alkalinity anomalies are observed, in some cases, few minor eruptive centers constitute low Sr/Y ratios, but high alkalinity (ex. Nealtica, Tetela), or even the contrary, high Sr/Y ratios, but low alkalinity (Cerro Xoyaca, Loma Tepenasco, La Joya next to Iztaccihuatl; [44]). Overall, the heterogeneity of the CVF monogenetic bodies decreases as it approaches the Popocatepetl-Iztaccihuatl stratovolcanoes. This distribution suggests the possibility that the CVF and the stratovolcanoes share the same mantle source which is a petrological evidence in literature [14, 44]. The contrast of Ba/Nb values between the stratovolcanoes and the center of CVF can be explained by different degrees of sediment contribution from the mantle [45], crustal assimilation (i.e. on Sr and Y; [39]), but also fractional crystallization, all having effects on the content of Ba and Nb [36].

### 1.4.3 Spatial heterogeneities of magma source

The most remarkable observation in the spatial model is the similarity with the geomarkers to the east CVF and the Popocatepetl-Iztaccihuatl complex. This could imply that since Quaternary, the magma source of many monogenetic conduits east of CVF and minor eruptive vents find similar magmatic source/a common root in the mantle in the vicinity of the polygenetic edifices (ex. La Hoya, [44]).

At the eastern limit of the mapped faults in [10], a similar N-S trending corridor is observed with high Ba/Nb anomalies. This includes the Pelagatos volcano mafic rocks despite the intermediate alkalinity and Sr/Y ratios (**Figures 3, 5**). Such signatures are associated to enriched mantle in incompatible elements. No regional faults are reported, and neither are lacustrine sediment covers east of Pelagatos [11]. A clear lineation of scoria cones is observed as shown by the point map overlays (**Figure 1**; Appendices). A E-W large scale change of crustal thickness can explain the variation, but Sr/Y do not show this N-S systematic association nor gradual changes along the direction of the Cocos plate subduction under the continent [8, 20].

A different dispersion pattern of the magma conduits could occur in this area due to complexity of cortical pathways for magma, but as the interpolation model and semi-variogram indicate (**Figure 4C**), individual plumbing systems of the monogenetic field must share a deep mantle source. Large-scale geochemical changes from all geomarkers do not correlate with the subducting slab geometry [8, 20, 34, 46], which point out that spatial heterogeneities of magma source rather increase where mantle interact with continental crust.

Monogenetic cones north and south of CVF are more mafic, less alkaline and many aligned scoria cones share the same rock composition (**Figures 3, 5**). Overall, monogenetic cones are spatially associated to E-W normal faults reported in the works of [16, 18] and recent mapping advances resumed in [10, 11]. Even though, no clear geochemistry (ex. Sr/Y) vs structural orientations associations are observed (**Figure 1**) contrary to some volcanic fields (minor eruptive centers along the Liquiñe-Ofqui Fault Zone, Southern Andes; [47, 48]). The normal fault systems in CVF also affect the crust below stratovolcanoes in addition to NE faults. This could imply to redirect orientations for magmas pathways and plumbing system depths. Thus, the extend of magma differentiation is variable and therefore the geochemistry of satellite monogenetic cones is modified to the polygenic edifices (i.e. Huililco monogenetic cones versus Llaima stratovolcano in Chile; [2]).

As for Nevado de Toluca, only Sta. Cruz and Tenango have remarkably similar trace element ratios (**Figures 4, 5**); Sr/Y as for Ba/Nb are associated to the high topography from SDLC. Overall, the western part of CVF constitutes spatial changes of geochemistry that vary over small areas. For example, near the flanks of the SDLC, rocks are more diverse in SiO<sub>2</sub> contents, have higher alkalinity and local interpolations show high Ba/Nb ratios [subduction signature). Then, further west, the same high Ba/Nb tendency follows a N-S corridor (Texontepec to Tezontle).

Local anomalies are various west of CVF and Tenango lateral fault system. Many E-W structures [11] do not correlate with the orientation of elongated polygons of high alkalinity and neither do they follow regional tendencies of spatial Sr/Y distribution (**Figure 3**). A more complex structural system can explain this difference according to the maps published in [1, 10, 49], which may imply contrasting basement lithologies (i.e. see [11, 50, 51]), crustal thickness or lithospheric fractures distinct in depth origin, movement and geometry in comparison to the Popocatepetl-Iztaccihuatl complex.

#### 1.5 Conclusion

The geostatistic and geographical mapping model of volcanic bulk rock chemistry in the Chichinautzion Volcanic Field (CVF) served as a methodological approach. Improve the comprehension of the spatial distribution of the magma heterogeneities inside a typical monogenetic volcanic field. The major methodological outcomes and geological explanations for such geochemical variations are resumed as follows:

1. The method presented here showed incertitude particularly for interpreting alkalis and Sr/Y lineation on the final models (**Figures 2, 3**). Limitations were encountered for assigning geographical coordinates, to control arbitrary parameters for spatial interpolation, to integrate physical environment parameters and to consider all strategical sampling objectives that may influence sample rock positions cumulated since 1948. The Moran Index (I) and the parameter Prob1Pnt helped to determine sample dispersion, which become mandatory to determine if some sectors inside a monogenetic field as CVF should be pre-

ferred for kriging, IDW or LD. It is consequently recommended to segment the area of study from monogenetic field and use the kriging method where a preferential sample orientation for high sample density cover is observed (satellite cones on the same flank from a polygenetic system, unidirectional topographic gradient, sampling along a lava flow or a structural lineation). Sectors where sample orientation is random and distribution is homogeneous should consider the Inverse Distance Weight (IDW) and Linear Decrease (LD).

- 2. The tectonic significance of high Ba/Nb geomarker is particularly of interest to indicate contribution of fluids derived from the subducted plate. This occurs in addition to the highly depleted mantle signature in the region of stratovolcanoes [21, 28, 29, 44]. One consideration is the presence of such anomalies related to amphibole fractioning [7] and even garnet from a deep source (~400 km; [27]). Another consideration is that such magmas are deeply sourced where hydrated fluids are produced by a metasomatized mantle source (from the slab, for example supported by [23, 29]). Despite of this association, such anomalies are geographically restricted to polygenetic systems. In addition, the Sr/Y ratio or alkalis geomarkers as Ba/Nb itself do not correlate with literature observations of the continental thickness [10, 11, 16, 18] nor the contact geometry of the subducted slab vs. lower continental crust [8, 20, 46]. Consequently, below CVF, rather than the slab influence [45], it is suggested that the role of lithospheric mantle–crust interaction is crucial to modify geochemical signature on the magmas feeding minor eruptive vents.
- 3. Shallow depth rigid continental crust (thickness and fractures) does not allow sufficient time and space for magmas to record subduction signature, therefore, the fast magma ascent feeding typical monogenetic systems do not easily record high Ba/Nb ratios [1]. In some cases, those magma could rather come from a fertile mantle, some with OIB signature, some hybrid depleted mantles [7, 9, 15, 21]. If this inference is correct, obstacles in the continental crust could be slowing down the frequent injection of new batches of magma feeding new minor eruptive vents around Iztaccihuatl-Popocatepetl, and Nevado de Toluca volcanic complexes. The plumbing system architecture of those stratovolcanoes already channel volumetric magmas derivated from a contrasting mantlecrust source.

#### Acknowledgements

The persons especially thanked for the technical support are Isaac Abimelec Farraz Montes (technician), Osvaldo Franco Ramos (student at Instituto de geografia, UNAM), and Laura Luna (technical secretary at Instituto de Geologia, UNAM). Dolores Ferres and Marie-Noël Guilbaud from Instituto de Geofisica (UNAM) reviewed datasets and gave important opinions about the methodology and the volcanological aspects of the work.

This work was supported by the Fonds de Recherche du Québec Nature et technologies (FRQNT) (Concours B1, Comité B4 (Maîtrise) who helped to support the Master program between 2010 and 2013 at Instituto de Geología, Universidad Nacional Autónoma de México (UNAM). The submission work process is supported by Conicyt Fondecyt Fondo Nacional de Desarrollo Científico y Tecnológico, with Project Code 11190846 attributed to Dr. Philippe Robidoux from Centro de Excelencia en Geotermia de los Andes (CEGA) and Departamento de Geología, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile.

# Appendices and nomenclature

# Appendice I Building the Geodatabase

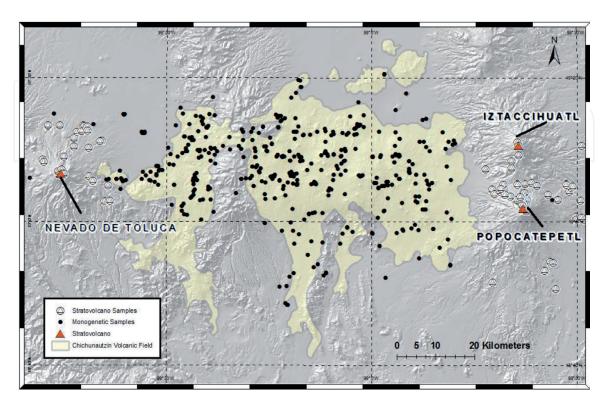


Figure A1.

Dispersion of the 583 samples in study (map modified from: Siebe et al., 2005; Siebe et al., 2004). The Chichinautzin Volcanic Field (CVF) is shown (shaded polygon) over the digital elevation model (DEM) from INEGI (2011). The big pale solid triangles represent the three well known stratovolcanoes and their associated samples (small solid black triangle). The small solid black circles represent the samples from the monogenetic cones of CVF.

Appendice II
Table of reference for samples used in the Geographic Information
System (GIS)

| Years | Complete reference  | ME  | RETE | Coord.      |
|-------|---|-----|------|-------------|
| 1948  | Arellano, A.R.V., 1948. La composicion de las<br>rocas volcanicas en la parte sur de la Cuenca<br>de Mejico, Boletin de la Sociedad Geologica<br>Mexicana, Tomo XIII, p.81-82, Cuadro 18                                  | Yes | No   | Description |
| 1975  | Whitford, D. J., Bloomfield K., 1975.<br>Geochemistry of late Cenozoic volcanic rocks<br>from the Nevado de Toluca area, Mexico, Year<br>Book Carnegie Inst. Washington 75 [1975], p.<br>207-213, #4571 in GERMS database | Yes | Yes  | Description |
| 1975  | Bloomfield, K. 1975, A late-Quaternary<br>monogenetic volcano field in central Mexico,<br>Aufsatze,Geologische Rundschau, 64:<br>p.476-499  | Yes | No   | Maps        |
| 1985  | Carrasco-Núñez, G., 1985. Estudio geológico<br>del Volcán Popocatépetl, BS thesis, México DF,<br>Facultad de Ingeniería, Universidad Nacional<br>Autónoma de México, 134p.  | Yes | No   | Description |

| 1987 | Nixon, Graham T., 1987. Petrology of the<br>Younger Andesites and Dacites of Iztaccihuatl<br>Volcano, Mexico: I. Disequilibrium Phenocryst<br>Assemblages as Indicators of Magma Chamber<br>Process, Journal of Petrology, Vol. 29, Part 2,<br>p. 213-368  | Yes | No  | Maps              |
|------|--|-----|-----|-------------------|
| 1989 | Pozzo, C. Ana Lillian Martin del Pozzo, 1989.<br>Geoquimica y paleomagnetismo de la sierra<br>Chichinautzin, Tesis que presenta la autor<br>en cumplimiento parcial de los requisitos del<br>grado Doctor en Ciencias (Geologia), Mexico<br>-D.F., 148 p.  | Yes | Yes | Maps              |
| 1989 | Swinamer, Ralph Terrance, 1989. The Geomorphology, Petrography, Geochemistry and Petrogenesis of the Volcanic Rocks in the Sierra Del Chichinautzin, Mexico, tesis submitted to the Department of Geological Sciences, in conformity with the requirements for the degree of Master Science, p.212                                     | Yes | Yes | Table             |
| 1995 | Cervantes, P., 1995. Eventos volcanicos al sur<br>de la Ciudad de Mexico, BS Thesis, México DF,<br>Facultad de Ingeniería, Universidad Nacional<br>Autónoma de México, 74p.  | Yes | Yes | Description       |
| 1998 | Arana Salinas, L., 1998. Geologia del volcan<br>Pelado, BS thesis, México DF, Facultad de<br>Ingeniería, Universidad Nacional Autónoma<br>de México, 57 p.   | Yes | Yes | Maps, description |
| 1998 | Delgado et al. 1998, Geology of Xitle Volcano<br>in southern Mexico City - A 2000 Year-Old<br>monogenetic volcano in an urban area, Revista<br>Mexicana e Ciencias Geologicas, volumen 15,<br>#2, 1998, p.115-131  | Yes | No  | Maps, description |
| 1998 | Romero Teran, Esther, 1998. Geologia<br>del Volcan Ajusco, BS thesis, Facultad de<br>Ingeneria, Universidad Nacional Autonoma de<br>Mexico (Instituto de Geofisica), 50 p.   | Yes | Yes | Maps              |
| 1999 | Verma S. P., 1999. Geochemistry of evolved magmas and their relationship to subduction-unrelated mafic volcanism at the volcanic front of the Central Mexican Volcanic Belt, Journal of Volcanology and Geothermal Research, Volume 93 [1999], p. 151-171, #3623 in GERMS database   | Yes | Yes | Table, maps       |
| 1999 | Arce S., Jose Luis, 1999. Reinterpretacion de<br>la erupcion pliniana que dio origen a la Pomez<br>Superior, Volcan Nevado de Toluca, Master<br>thesis: Maestro en Sismologia y Fisica del<br>interior de la Tierra, Postgrado en ciencias de<br>la tierra, Universidad Autonoma Nacional de<br>Mexico (Instituto de Geofisica), 92 p. | Yes | Yes | Maps, description |
| 1999 | Wallace, P., and I. Carmichael (1999), Quaternary volcanism near the valley of Mexico: Implications for the subduction zone magmatism and the effects of crustal thickness variations on primitive magma compositions, Contribution to Mineralogy and Petrology, vol. 135, p.291-314   | Yes | Yes | Table, maps       |

| 2000 | Verma, P. Surendra, 2000. Geochemistry of<br>the subducting Cocos plate and the origin of<br>subduction-unrelated mafic volcanism at the<br>volcanic front of the central Mexican Volcanic<br>Belt, Geological Society of America, Special<br>Paper 534, p.195-222   | Yes | Yes | Table, maps,<br>description |
|------|--|-----|-----|-----------------------------|
| 2000 | Gonzalez Huesca, Alberto, 2000. Estudios de<br>detalle estratigrafico y sedimentologico del<br>Lahar de San Nicolas en el flanco noreste del<br>volcan Popocatepetl, BS thesis, Facultad de<br>Ingeneria, Universidad Nacional Autonoma de<br>Mexico, 110 p.   | Yes | No  | Maps                        |
| 2001 | Straub, S. M., Martin-Del Pozzo, A. L., 2001. The significance of phenocryst diversity in tephra from recent eruptions at Popocatepetl volcano (Mexico), Contrib. Mineral. Petrol. 140 [2001], p. 487-510, #3506 in GERMS database   | Yes | Yes | Description                 |
| 2001 | Cervantes de la Cruz., Karina Elizabeth,<br>2001. La pomez blanca intermedia: deposito<br>producido por una erupcion plinana-<br>subpliniana del volcan Nevado de Toluca hace<br>12,100 anos, Master's thesis, Postgrado en<br>Ciencias de la Tierra, Universidad Nacional<br>Autonoma de Mexico, 84 p.  | Yes | Yes | Description,<br>maps        |
| 2001 | Velasco Tapia, Fernando, 2001. Aspectos geoestadisticos en geoquimica analitica: Applicacion en el modelado geoquimico e isotopico de la sierra de Chichinautzin, Cinturon Volcanico Mexicano, Phd thesis: Doctor en ciencias (geoquimica), Postgrado en ciencias de la tierra, Universidad Nacional Autonoma de Mexico (Instituto de Geofisica), 273 p. | Yes | Yes | Table, maps                 |
| 2004 | Siebe, Claus, Rodriguez-Lara, V., Schaaf, P., Abrams M., 2004. Geochemistry, Sr-Nd isotope composition and tectonic setting of Holocene Pelado, Guespalapa and Chichinautzin scoria cones, south of Mexico City, Journal of Volcanology and Geothermal Research, Volume 130 [2004], p. 197-226, #6862 in GERMS database                                  | Yes | Yes | Table, maps                 |
| 2004 | Arana Salinas, L., 2004. Geologia de los volcanes monogeneticos Teuhtli, Tlaloc, Tlacotenco, Ocusacayo y Cuauhtzin en la Sierra Chichinautzin, al Sur de la Ciudad de Mexico, Master's thesis (Vulcanologia), Postgrado en Ciencias de la Tierra, Universidad Nacional Autonoma de Mexico, 117 p.  | Yes | Yes | Maps, descriptio            |
| 2004 | Raymundo G. Martinez-Serrano et al., 2004.<br>Sr, Nd and Pb isotope and geochemical<br>data from the Quaternary Nevado de<br>Toluca volcano, a source of recent adakitic<br>magmatism, and the Tenango Volcanic<br>Field, Mexico, Journal of Volcanology and<br>Geothermal Research, Volume 138, Issues 1-2,<br>15 November 2004, p.77-110               | Yes | Yes | Table, maps                 |

| 2005 | Witter J. B., Kress V. C., Newhall C. G., 2005.  | Yes | Yes | Description          |
|------|--|-----|-----|----------------------|
|      | Volcan Popocatepetl, Mexico. Petrology,<br>Magma Mixing, And Immediate Sources Of<br>Volatiles For The 1994-Present Eruption, J.<br>Petrol. 46 [2005], p. 2337-2366, #8497 in<br>Germs database  |     |     |                      |
| 2005 | Schaaf, Peter, Jim Stimac, Claus Siebes and Jose Luis Macias, 2005. Geochemical Evidence for Mantle Origin and Crustal Processes in Volcanic Rocks from Popocatépetl and Surrounding Monogenetic Volcanoe; Central Mexico, Journal of Petrology, Volume 46, #6, p. 1243-1282   | Yes | Yes | Table                |
| 2006 | Ceballos, Giovanni Sosa, 2006. El Paleo-<br>Popocatepetl: petrologia, geoquimica e<br>isotopia de secuencias pre 23, 000 anos,<br>Master's thesis, Postgrado en Ciencias de la<br>Tierra, Universidad Nacional Autonoma de<br>Mexico (Colegio de Geografia), 120 p.  | Yes | Yes | Description,<br>maps |
| 2008 | Antonio, Marco, 2008. Reconstrucción del evento eruptivo asociado al emplazamiento del flujo piroclástico El Refugio hace 13 ka, volcán Nevado de Toluca (México), Revista Mexicana de Ciencias Geologicas, V.25, # 1, 2008, p.115-147   | Yes | Yes | Description,<br>maps |
| 2008 | Meriggi, Lorenzo, José Luis Macías, Simone<br>Tommasini, 2008. Heterogeneous magmas<br>of the Quaternary Sierra Chichinautzin<br>volcanic field (central Mexico): the role of<br>an amphibole-bearing mantle and magmatic<br>evolution processes, HeterRevista Mexicana de<br>Ciencias Geológicas, v. 25, #.2, p. 197-216                              | Yes | Yes | Table                |
| 2008 | Straub, S. M., Martin-Del Pozzo, A. L.,<br>Langmuir, C.H., 2008. Evidence from<br>High-Ni Olivines for a Hybridized peridotite/<br>pyroxenite source for orogenic andesites<br>from the central Mexican volcanic belt;<br>Geochemistry Geophysics Geosystems 9, 33 p.  | Yes | Yes | Table                |
| 2009 | Guilbaud, MN., Siebe, C., Agustín-Flores, J., 2009. Eruptive style of the young high-Mg basaltic-andesite Pelagatos scoria cone southeast of México City. Bull. Volcanol. 71, 859–880.   | Yes | Yes | Table, maps          |
| 2009 | Augustin Flores, Javier, 2009. Geologia y petrogenesis de los volcanes monogeneticos Pelagatos, Cerro del Agua y Dos Cerros en la Sierra Chichinautzin, al sur de la Ciudad de Mexico, Master thesis: Maestria en Ciencias (Vulcanologia), Postgrado en Ciencias de la Tierra, Universidad Nacional Autonoma de Mexico (Instituto de Geofisica), 97 p. | Yes | Yes | Table                |
| 2010 | Arana-Salinas, L., Claus Siebe and José Luis<br>Macias 2010. Dynamics of the ca. 4965 yr<br>14C BP "Ochre Pumice" Plinian eruption<br>of Popocatepetl volcano, Mexico, Journal<br>of Volcanology and Geothermal Research,<br>Volume 192, Issues 3-4, 10 May 2010, p.<br>212-228  | Yes | Yes | Description          |

| 2011 | Augustin-Flores, Javier, Claus Siebe and Marie-Noëlle Guilbaud, 2011. Geology and geochemistry of Pelagatos, Cerro del Agua, and Dos Cerros monogenetic volcanoes in the Sierra Chichinautzin Volcanic Field, south of Mexico City, Journal of Volcanology and | Yes | Yes | Table |  |
|------|--|-----|-----|-------|--|
|      | Geothermal Research, Volume 201, Issues 1-4, 15 April 2011, p.143-162  |     |     |       |  |

#### Table A1.

It is specified if major elements (ME) or Rare Earth and Trace Elements (RETE) are available from the references. Coordinates (Coord.) are taken from tables, maps or interpreted from description in the text.

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