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ORIGINAL PAPER

Hydrothermal alteration of surficial rocks at Los Humeros geothermal field, Mexico: a magnetic susceptibility approach

Kailasa Pandarinath[1] · Jessica Liliana Rivas-Hernández[2] · José Alberto Arriaga-Fuentes[2] · David Yáñez-Dávila[3] · Eduardo González-Partida[4] · E. Santoyo[1]

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Abstract

Utility of the geothermal surface manifestations (GSMs; thermal springs, geysers, fumaroles, and zones of hydrothermal alteration) in the studies related to the geothermal exploration is widely recognized. The identification of hydrothermally altered rocks and zones of alteration is very important because their presence indicates the type and size of the geothermal reservoir and existing thermal conditions. The use of traditional methods (i.e., geochemistry, mineralogy, and petrography) requires expensive equipment, time-consuming, and laborious sample preparation methods. Some of the rock magnetic parameters, like magnetic susceptibility (χlf) and percentage of frequency-dependent magnetic susceptibility (χfd%), are potential to become effective additional tools in identification of the hydrothermal rocks during the initial stages of geothermal exploration. Three chemical methods, Chemical Index of Alteration (CIA), loss-on-ignition (LOI), and the binary plot ($CaO + Na_2O + K_2O$) vs. ($Fe_2O_3 + MnO + MgO$), along with two rock magnetic methods, χlf and the binary plot (χlf vs. χfd%), are applied to nine intensively altered andesite reference rocks. All the five methods have correctly identified that 99 out of the total 350 studied rocks are altered. More altered rocks are distributed surrounding the several faults in the study area. Various faults (e.g., Los Humeros fault and the Loma Blanca fault) favor fluid flow and present strong hydrothermal alteration at the surface. However, there are no altered rocks on the surface region between the E-W trending Las Papas and Las Viboras faults. The presence of only the deeper fluid pathway toward the east in the surroundings of these two faults result into the almost absence of hydrothermal alteration along their strike at the surface. Consequently, there are not many altered rocks observed surroundings these two faults at the surface. These features suggest that the surface hydrothermal alteration at Los Humeros Geothermal Field (LHGF) is controlled by faults. χlf and χfd% are reliable, simple to measure, fast, cost-effective, and have the potential to become reliable additional tools for future exploration studies.

Keywords Geothermal energy · Los Humeros geothermal field · Geothermal prospection · Rock magnetic properties · Grain size and faults · Geothermal structures

Introduction

Geothermal energy is produced from heat below the Earth's surface. The information on the quantity and depth of the heat source in the region can be obtained by the studies on

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✉ Kailasa Pandarinath
pk@ier.unam.mx

[1] Instituto de Energías Renovables, Universidad Nacional Autónoma de México, Privada Xochicalco -S/N, Centro, 62580 Temixco, Morelos, México

[2] Escuela Superior de Ciencias de La Tierra, Ex-Hacienda de San Juan Bautista, Taxco El Viejo, 40323 Taxco El Viejo, Guerrero, Mexico

[3] Posgrado en Ingeniería, Instituto de Energías Renovables, Universidad Nacional Autónoma de México, Privada Xochicalco S/N, Centro, 62580 Temixco, Morelos, México

[4] Centro de Geociencias, Universidad Nacional Autónoma de México, Campus Juriquilla, 76230 Santiago de Querétaro, México

the surface manifestations such as thermal springs, geysers, fumaroles, volcanos, hydrothermally altered rocks, and zones of hydrothermal alteration. Due to this reason, the utility of these geothermal surface manifestations (GSMs) in the studies related to the geothermal exploration is widely recognized. The interaction of thermal waters with surface rocks results in dissolution of primary minerals and precipitation of new minerals known as hydrothermal (secondary) minerals (Nicholson 1993). The distribution of hydrothermally altered rocks depends on the composition of primary minerals, the water–rock interaction, the deep temperature of the geothermal reservoir, size of the geothermal system, and the thermal (boiling and dilution) conditions prevailing at the region (Reed and Spycher 1984). The main objective of the geothermal surface exploration is to estimate the resources and characteristics of the geothermal systems before carrying out the drilling of geothermal wells. Hence, the identification, mapping, and evaluation of these surface manifestations are crucial for the evaluation of the geothermal potential of an area.

Several GSMs, especially thermal springs, geysers, fumaroles, and hydrothermally altered rocks and zones of alteration, are extensively studied by petrographic, mineralogical, and geochemical methods (Hopf 1993; Fulignati et al. 1999; Verma et al. 2018; Pandarinath et al. 2020). Apart from these methods, magnetic susceptibility (Pandarinath et al. 2014, 2019) and various chemical alteration indices ($n=47$; Pandarinath 2022) are also considered as reliable methods in the geothermal exploration studies. The geochemical (e.g., mass and concentration changes, weathering/alteration indices), mineralogical (identification and semi-quantification of minerals by XRD), and petrographic (e.g., identification of fresh and alteration mineralogy, level of alteration) methods have been historically applied to identify hydrothermally altered rocks and zones of hydrothermal alteration. More recently, magnetic susceptibility of rocks has been successfully applied in the identification of altered rocks from drilled geothermal wells of Los Azufres geothermal field (LAGF; Pandarinath et al. 2014). Here, the hydrothermal alteration status (fresh or altered) identified for these well rocks by magnetic susceptibility (χlf) values is confirmed by comparing with the alteration status obtained by other reliable and extensively applied methods (mineralogy, petrography, grade of hydrothermal alteration).

Apart from χlf, another rock magnetic parameter, the percentage frequency-dependent magnetic susceptibility (χfd%), may also be a useful parameter in the identification of hydrothermally altered rocks and zones of alteration. χfd% indicates the presence of ultrafine superparamagnetic particles (SPs; Thompson and Oldfield 1986; Jackson et al. 1993; Walden 1999), and it is a measure of occurrence of very fine magnetic domains on the superparamagnetic particle (SP) to stable single domain (SSD). Dearing et al. (1996, 1997) have reported that χfd% value of <3 and χlf $>0.5\times10^{-6}$ m^3 kg^{-1} indicate that there are no SP grains, and the magnetic mineral assemblage is dominated by multiple domain (MD) and SSD grains. The proportions of MD-SSD grains are higher in the altered rocks than in the unaltered rocks (Long et al. 2015; Nédélec et al. 2015).

Apart from this, there is a need of further testing the systematic applicability, consistency, and reliability of χlf and χfd% for the rocks representing the different tectonic settings, different thermal and fluid flow conditions, and different types of geothermal fields. In this perspective, though the rock magnetic parameters are already successfully applied for the drilled well rock cuttings of the liquid-dominated LAGF (Pandarinath et al. 2014; 2019), it is necessary to check their applicability for the rocks of a vapor-dominated geothermal fields. In view of this, the super-hot vapor-dominated Los Humeros geothermal field (LHGF; González-Partida et al. 2022) is selected for the present study. At present, the geothermal industry needs new reliable methods simple to measure, fast, and cost-effective. The χlf and χfd% are effective and low-cost tools in identification of the hydrothermal rocks during the initial stages of geothermal exploration. The successful application of rock magnetic methods is potentially useful for mineral exploration in areas where mineralization is associated with altered rocks. To achieve this, the present work is carried out with an objective to evaluate the performance of χlf and χfd% in identification of the zones of hydrothermal alteration by comparing with the results obtained by geochemical methods [CIA, LOI, binary plot of ($CaO+Na_2O+K_2O$) vs. ($Fe_2O_3+MnO+MgO$)].

Hereafter, in this work, magnetic susceptibility measured at low frequency (χlf) is referred to as magnetic susceptibility.

Lithology of the study area

The basement of the LHGF consists of limestone sequences of Late Cretaceous age (e.g., Viniegra 1965). Andesites, dacites, rhyodacites, rhyolitic tuffs, rhyolites, and some basaltic rocks overlie this basement formations. Andesite and pre-caldera volcanic rocks dated at 3.5 Ma and 1.55 Ma are exposed outside the caldera (Ferriz and Mahood 1984). More details on the geology of the LHGF area are extensively reported in the pioneer works reported in the literature (e.g., Ferriz and Mahood 1984; Negedank et al. 1985; Gutiérrez-Negrín and Izquíerdo-Montalvo 2010; Carrasco-Núñez et al. 2012, 2015, 2017, 2018, 2021).

Methodology

A total of 350 rock samples from the surface area of the Los Humeros Geothermal Field (LHGF; Fig. 1) were collected with recording of all the necessary field information (latitude, longitude, the field observations on the lithology, etc.). The differentiation of the altered and fresh rocks is carried out based on the visual observations recorded in the field with the help of hand magnifying lens. The altered rocks were identified by the following: their aphanitic texture, reddish/yellowish color due to the iron oxides, the surface of the rocks can be easily scratched by thumbnail and pocketknife, complete destruction of the original rock texture, can be broken into smaller pieces by hand, dominated by clay (very fine grains), and strong odor of sulfur (presence of sulfur minerals). The rocks were considered as fresh, if the observations are contrary to those mentioned above for altered rocks. The rock type is obtained by plotting its location (latitude and longitude) in the recently updated geologic map of Carrasco-Núñez et al. (2017) and the rock formation in which it is ubicated. The obtained rock types are 59 basalts, 11 rhyolites, 48 trachyandesites, 50 trachytes, and 182 tuffs (Table 1).

Nine intensively altered andesite rocks from the well Az-26 of LAGF are selected as a representative for hydrothermally altered rocks. Major element data for the nine andesite rocks is obtained from Torres-Alvarado and Satir (1998). χlf values of these 9 rocks vary between 0.37 and $11.2 \times 10^{-6}\ m^3\ kg^{-1}$ (Pandarinath et al. 2014, 2019). Validity of the application of χlf and χfd% in identification of hydrothermally altered rocks and zones of hydrothermal alteration is carried out by comparing their performances in the identification of the hydrothermal alteration of the rock samples whose alteration status is obtained by other established and well-known methods. The geochemical and rock magnetic data for these andesite rocks were compiled from Torres-Alvarado and Satir (1998) and Pandarinath et al. (2014, 2019), respectively.

CIA is proposed by Nesbitt and Young (1982), and it is presently the most widely being used chemical index to identify the intensity of alteration in several areas of research.

The equation proposed to calculate the CIA is shown below:

$$CIA = \left(\frac{Al_2O_3}{Al_2O_3 + CaO^* + Na_2O + K_2O} \right) \times 100$$

where the concentrations are in molecular proportion and CaO* is the amount of CaO incorporated in the silicate fraction of the rocks.

LOI data for the nine andesite rocks was obtained from Torres-Alvarado and Satir (1998). Apart from this, LOI data from three US Geological Survey standard reference materials RGM-1 (rhyolite), AGV-1 (andesite), and BCR-1 (basalt) was also compiled from Lechler and Desilets (1987). They have reported that 0.99, 1.62, and 0.58%, respectively, are observed values and 1.13, 1.85, and 1.67, respectively, are the corrected values, for the standards RGM-1, AGV-1 (AGV-2), and BCR-1. Generally, these standards are considered as fresh and their reported LOI values are taken as representative samples for fresh rocks in this work. A major element based binary plot of ($CaO + Na_2O + K_2O$) versus ($Fe_2O_3 + MnO + MgO$) has successfully demarcated the altered and fresh rocks.

Similarly, methodologies for the estimation of magnetic susceptibility (χlf), percentage frequency-dependent magnetic susceptibility (χfd%), and binary plots of χlf vs. χfd% are briefly presented below.

Magnetic susceptibility is measured at low (0.47 kHz; χ_{lf}) and high (4.7 kHz; χ_{hf}) frequencies on a calibrated Bartington Susceptibility Meter (Model MS2B) with a dual frequency sensor. The frequency-dependent magnetic susceptibility (χfd) was calculated as absolute frequency dependence as (χfd) = χlf—χhf, and relative frequency dependence, χfd (%) = ((χlf − χhf) / χlf)*100, where χlf and χhf are measured at low and high frequency, respectively. χlf and χhf are measured and χfd% is calculated for all 350 surface rock samples from LHGF. Lower χfd% values and/or higher proportions of SD (or SSD) grains are characteristic of relatively more altered rocks.

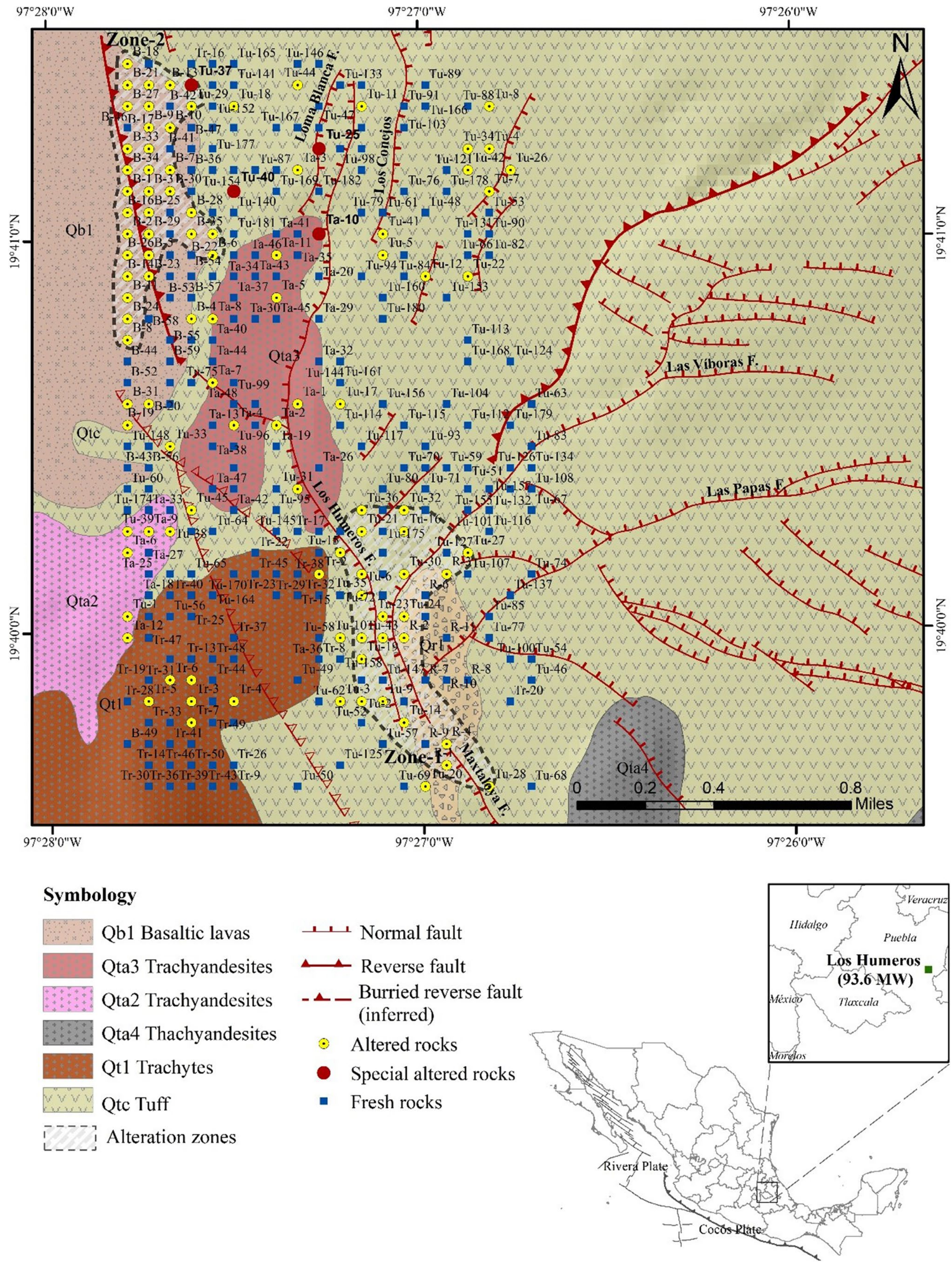
Hereafter, magnetic susceptibility measured at low frequency (0.47 kHz) is referred to as magnetic susceptibility (χlf).

Results

In this work, the identification of altered rocks and the zones of hydrothermal alteration at the surface region of LHGF has been carried out based on the following work plan:

Selection of hydrothermally altered reference rocks

Nine intensively altered andesite rocks collected from different depths of the well Az-26 of LAGF were selected as a reference for hydrothermally altered rocks. These rocks were extensively studied for petrography (González-Partida et al. 1989, 2000; Torres-Alvarado 1996), chemical (Cathelineau et al. 1987; Torres-Alvarado and Satir 1998), mineralogical analyses (Cathelineau et al. 1985; González-Partida et al. 1989, 2000), and rock magnetic parameters (Pandarinath et al. 2014, 2019; Pandarinath 2022). All these studies have dealt with the hydrothermal alteration and indicated that the rocks collected from different depths from the well Az-26 of LAGF were hydrothermally altered. By considering these integrating studies, 9 rocks from the well Az-26 were selected as a reference for hydrothermally altered rocks.


97°28'0"W
97°27'0"W
97°26'0"W
19°41'0"N
19°40'0"N
N
Zone-2
Zone-1
Qb1
Qtc
Qta2
Qta3
Qt1
Qr1
Qta4
Loma Blanca F.
Los Conejos
Los Humeros F.
Maxtaloya F.
Las Víboras F.
Las Papas F.
0 0.2 0.4 0.8 Miles
Symbology
Qb1 Basaltic lavas
Qta3 Trachyandesites
Qta2 Trachyandesites
Qta4 Thachyandesites
Qt1 Trachytes
Qtc Tuff
Alteration zones
Normal fault
Reverse fault
Burried reverse fault (inferred)
Altered rocks
Special altered rocks
Fresh rocks
Veracruz
Hidalgo
Puebla
Los Humeros (93.6 MW)
México
Tlaxcala
Morelos
Rivera Plate
Cocos Plate

◂**Fig. 1** Map showing the locations of the surface rock samples studied in this work, along with the geology and fault features at the Los Humeros Geothermal Field, Mexico (modified from Carrasco-Núñez et al. 2017; some fault features also taken from Jentsch et al. 2020). The identification of the hydrothermal alteration zones (Zone 1 and Zone 2) are results of the present work. The rocks represented by filled-in circles with yellow color are altered rocks ($n=99$) and the filled-in squares with blue color are fresh (least-altered) rocks ($n=251$). The circles with yellow color and numbered B-1 to B-35, R-1 to R-4, Ta-1 to Ta-11, Tr-1 to Tr-7, and Tu-1 to Tu-43, respectively, are altered basalts (35), rhyolites (4), trachyandesites (11), trachytes (7), and tuffs (42). The circles with yellow color and numbered B-36 to B-59, R-5 to R-11, Ta-13 to Ta-48, Tr-8 to Tr-50, and Tu-46 to Tu-182, respectively, are fresh (least-altered) basalts (24), rhyolites (7), trachyandesites (37), trachytes (43), and tuffs (140)

Applicability of the geochemical methods in identification of hydrothermal alteration in volcanic rocks

There are several geochemical methods (e.g., mobility of elements, change in mass, concentration changes) traditionally applied in identification of altered rocks. In addition to these established methods, some geochemical parameters were recently identified as simple and reliable methods (e.g., CIA, LOI, and major element oxides composition, Pandarinath 2022) in the identification of altered rocks. To establish these methods as reliable in identification of altered rocks of the surface areas and from the geothermal wells, it is necessary to further validate the applications for the different types of alteration and thermal conditions prevailing in different geothermal fields.

Chemical Index of Alteration (CIA)

CIA is proposed by Nesbitt and Young (1982). It is calculated for the 9 andesite rocks by using the major elements composition data obtained from Torres-Alvarado and Satir (1998). The rocks with CIA values < 60 were considered as fresh rocks, whereas CIA values > 60 are characteristics of altered rocks (Nesbitt and Young 1982, 1984; McLennan et al 1993). The calculated CIA values for 9 andesite rocks vary between 65.8 and 77.7% (Fig. 2 a). The calculation of CIA for the chemical data of a US Geological Survey standard reference materials AGV-2 (andesite) has provided a value of 45.7. As the CIA value of this standard rock is of < 60, it is therefore considered as a fresh rock sample. As AGV-2 is a USGS standard reference for fresh andesite rock, and the calculated CIA value of 45.7 also indicates that it is a fresh rock. CIA values of all the nine andesite rocks are > 60%, which indicates the all the nine are altered rocks, whereas AGV-2 is a fresh andesite standard rock (Fig. 2 a).

Loss-on-ignition (LOI)

LOI is proposed by Sueoka et al. 1985; as mentioned by Irfan 1996). Measurement of LOI may be useful in certain geologic studies as an actual estimate of total volatiles, for instance, as an indication of volcanic rock alteration resulting from hydration or calcification of mafic minerals. LOI content of the volcanic rocks is directly proportional to the moisture content. It indicates the H_2O^+ content in a sample (in weight) when it is heated at 105 °C (Irfan 1994a, 1994b; Ng et al. 2001). As LOI reflects H_2O^+ content in a sample, an increase of H_2O^+ is caused by the hydration and clay formation during weathering causes an increase in H_2O^+ + /LOI and, thus, is sensitive to the weathering process under humid conditions. LOI is directly proportional to the intensity of alteration; the higher the LOI value, the more is the intensity of alteration (Suoeka et al. 1985; Ng et al. 2001). For fresh rocks, LOI values are < 2%, whereas values > 2% correspond to altered rocks (Le Bas et al. 1986; Harijoko et al. 2010). Lechler and Desilets (1987) have reported a corrected LOI value of 1.85% for the USGS AGV-2 (andesite), and consider LOI values < 1.85% for fresh/least altered andesite rocks.

In the present work, LOI values of the 9 andesite rocks vary between 4.65 and 9.0% (Torres-Alvarado and Satir 1998). Its values increase with an increase in the intensity of alteration. In the present work, LOI values of all 9 andesite rocks are much higher (varies between 4.65 and 9.0%) than LOI value 1.85% of the USGS standard reference rock AGV-2 (andesite). Therefore, all 9 andesite rocks may be considered as altered rocks (Fig. 2 b).

Binary plot ($CaO + K_2O + Na_2O$) vs. ($Fe_2O_3^T + MnO + MgO$)

Another method that can be used to differentiate the fresh and altered rocks is a binary plot (Fig. 2 d) based on their major element composition [($CaO + K_2O + Na_2O$) vs. ($Fe_2O_3^T + MnO + MgO$)]. Here, the major element component ($CaO + K_2O + Na_2O$) and ($Fe_2O_3^T + MnO + MgO$) of felsic (X-axis) and mafic minerals (Y-axis) in volcanic rocks, respectively. Felsic refers to silicate minerals (high in light-colored minerals; e.g., feldspar and quartz), which contain the major elements Ca, K, and Na, whereas mafic refers to minerals (high in dark-colored minerals; e.g., pyroxene, amphibole, olivine, and mica), which contain the elements Fe, Mn, and Mg (Armstrong-Altrin 2020; Armstrong-Altrin et al 2022). The intensive alteration of the volcanic rocks results in dissolution of these felsic and mafic minerals and causes the loss in the contents of the mobile major elements Na, K, Ca, Fe, Mn, and Mg. Nesbitt and Young (1982) have reported that Ca, Na, and K contents must decrease as the intensity of weathering/alteration increases. Babechuk et al.

Table 1 Magnetic susceptibility values measured at low (χ_{lf}) and high (χ_{hf}) frequencies and the percentage frequency-dependent susceptibility (χ_{fd} %) in different rock types from the surface of Los Humeros geothermal field

Rock type	No. of samples (n)	χ_{lf} (10^{-6} m^3 kg^{-1}) Mean	χ_{lf} (10^{-6} m^3 kg^{-1}) Minimum	χ_{lf} (10^{-6} m^3 kg^{-1}) Maximum	χ_{hf} (10^{-6} m^3 kg^{-1}) Mean	χ_{fd} (%)Mean
Basalts	59	1.93 0.2–44	0.05	5.40	1.88	3.50
Rhyolites	11	1.97 0.014–13	0.76	7.18	1.92	3.46
Trachyandesites	48	2.13	0.05	9.48	2.03	5.57
Trachytes	50	1.55	0.07	5.47	1.48	5.00
Tuffs	182	1.95	0.02	11.05	1.86	4.66
Total	350					

(2014) have reported that alteration of mafic substrates has resulted into a net loss of the mobile major elements (Ca, Mg, Na, K, and Fe). Similar alteration-induced loss in the contents of CaO, Na_2O, K_2O, Fe_2O_3, MnO, and MgO are also indicated in the surface acid rocks of the Acoculco geothermal field by Pandarinath et al. (2020). In the present study, to validate the binary plot, along with the 9 andesite rock samples, 8 known fresh/least-altered rocks (3 igneous rocks of average composition of the Earth, red-colored star symbols in Fig. 2 d, Clarke and Washington 1922; and 5 surface fresh andesite rocks of LAGF, green-colored inverted triangle symbols, Cathelineau et al. (1985), Torres-Alvarado and Satir (1998) and 10 intensively altered volcanic rocks (3 blue-colored star symbols, Gifkins et al. 2005, and 7 black-colored triangle symbols, felsic altered rocks from 0 to 440 m depth of the well Az-26 of LAGF, Torres-Alvarado and Satir (1998) are also plotted. In this binary plot, all 8 known fresh rocks are plotted away from the origin of the plot (Gr-1 in Fig. 2 d). Among the plotted 10 altered felsic rocks, 7 altered rocks are plotted near to the origin and are near to the X-axis (Gr-3), whereas 2 out of the 3 intensively altered volcanic rocks (Gr-4 in Fig. 2 d) have plotted towards the origin of the plot and near to the Y-axis, and one intensively altered volcanic rock very near to the origin of the plot. The plotted locations of all the fresh ($n=8$; Gr-1) and altered rocks ($n=10$; Gr-3 and Gr-4) in Fig. 2 are in accordance with their known alteration status. This shows the reliability of this binary plot in the identification of fresh and altered rocks. Now, regarding 9 andesite rocks, whose alteration status is being identified in this work, in this binary plot shows that 7 rocks are plotted as a group (Gr-2 in Fig. 2 d) towards the origin of the plot, whereas the remaining 2 rocks are plotted along with the fresh rocks in the group Gr-1 (Fig. 2 d). This indicate that the 7 rocks are intensively altered, and the remaining 2 rocks are fresh. However, these two rocks also showing the similar distribution trends (almost equidistance to the X-axis and Y-axis) and nearer to the group of the 7 rocks, these 2 rocks may not be considered as very different to these 7 rocks (less altered?). Located at almost equidistance to the X-axis and Y-axis may indicate that these andesite rocks are altered rocks (with two of them are less altered) and their chemical composition is intermediate (neither felsic nor mafic).

All the three abovementioned geochemical methods have correctly identified the nine reference andesite rocks as altered rocks. This confirms the applicability of these three geochemical methods in identification of hydrothermal alteration in volcanic rocks.

Applicability of two rock magnetic methods in identification of hydrothermal alteration in the volcanic rocks

Applicability of χlf in identification of altered rocks

Recently, χlf is successfully applied in identification of altered rocks from the geothermal wells (Az-26 and Az-49) from LAGF (Pandarinath et al. 2014, 2019). To establish χlf as a reliable method in the identification of altered rocks, it is necessary to further validate its applicability for the different types of alteration and thermal conditions prevailing in different geothermal fields.

Nine andesite rocks are obtained from different depths in Well Az-26 of LAGF, and their alteration status is confirmed as intensively altered rocks by the studies of petrography and mineralogy (Torres-Alvarado and Satir 1998) and magnetic susceptibility (Pandarinath et al. 2014). In these studies, it is observed that as the depth of the well increases, there is an increase in the reservoir temperature and hydrothermal alteration, and there is a decrease in the concentrations of Fe–Mg silicates and opaque minerals. The decrease in χlf, and Fe–Mg mineral contents with an increase in the hydrothermal alteration degree, pyrite, and hematite contents (see Fig. 2 of Pandarinath et al. 2014) suggests the hydrothermal alteration of ilmenite (occuring as a opaques) and Fe–Mg minerals (characteristic of high χlf values) to pyrite, hematite, and other opaque minerals (with low χlf values). This shows that hydrothermal alteration of the rocks results in dissolution of magnetic minerals and lower χlf values.

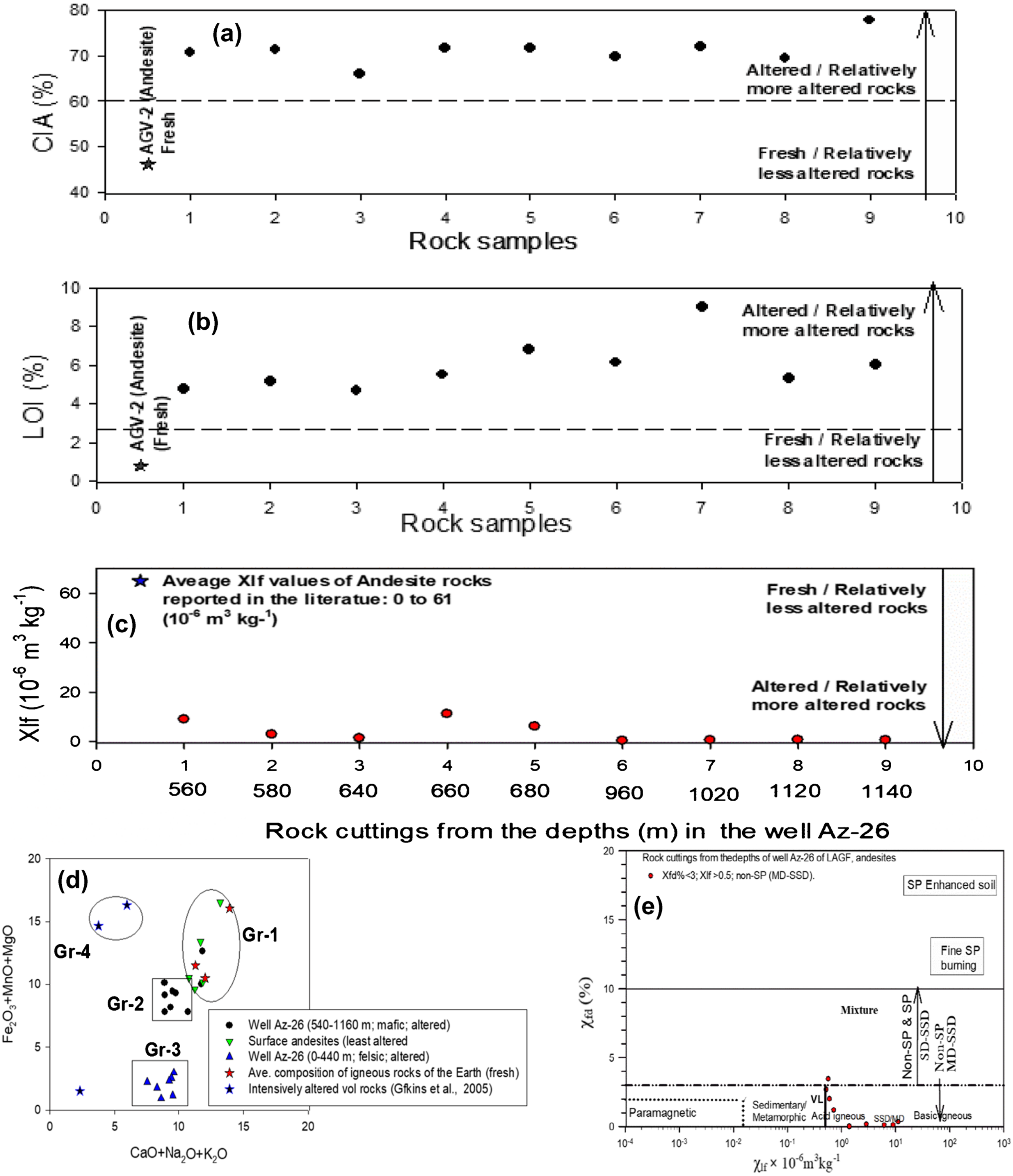


Fig. 2 Showing the applicability of chemical and the rock magnetic parameters in identification of altered rocks by applying for the andesite rocks with known alteration status [**a** CIA, **b** LOI, **c** χlf, **d** plot of ($CaO + K_2O + Na_2O$) Vs ($Fe_2O_3T + MnO + MgO$), and **e** binary plot of (χlf Vs χfd%)]

The nine andesite rocks representing the deeper depth of the well Az-26 are selected as a reference for an intensively altered rocks. χlf values of these rocks vary between 0.37 and 11.2×10^{-6} m^3 kg^{-1} (Pandarinath et al. 2014). An average χlf value of fresh andesite rocks reported in the literature vary between 0 and 61×10^{-6} m^3 kg^{-1} (Hunt et al. 1995). The rocks which have undergone high intensity of alteration results in lower χlf values. This validates the applicability of χlf in identification of altered rocks.

The interaction of hydrothermal fluids with rocks results in the hydrothermal alteration of primary minerals. In a geothermal area, an anomaly of low magnetic susceptibility values of rocks in a homogenous litho unit characterized by high magnetic susceptibility may suggest hydrothermal alteration.

Applicability of χlf vs. χfd% in identification of hydrothermally altered rocks and zones of hydrothermal alteration

The nine andesite rock samples are plotted in the binary diagram χlf versus χfd% of Dearing et al. (1996). χlf and χfd% values of these andesite rocks vary from 0.52×10^{-6} m^3 kg^{-1} to 11.2×10^{-6} m^3 kg^{-1} and from 0 to 3.44%, respectively (Fig. 2 c). Eight out of the nine rocks have plotted in the zone with χ_{fd} values of < 3% (non-SP; Fig. 2 e). Even the ninth sample, which has indicated χfd% value of 3.44%, is 0.44% higher than the boundary value of 3%. In the case of χlf, all nine andesite rocks have indicated the χlf values of > 0.5×0^{-6} m^3 kg^{-1} (Fig. 2c). Therefore, it may be considered that all 9 andesite rocks have χ_{fd}% values of < 3 and $\chi lf > 0.5 \times 10^{-6} m^3 kg^{-1}$. This indicates that there are no SP grains, and the magnetic mineral assemblage is dominated by MD and SSD grains (Dearing et al. 1997, 2001). The rocks with higher proportions of MD and SSD grains are indicative of relatively more alteration.

The abovementioned two rock magnetic methods have correctly identified the nine reference andesite rocks as altered rocks. This shows the validation of the applicability of the abovementioned three geochemical and two rock magnetic parameters in identification of hydrothermally altered rocks.

Applicability of χlf in the identification of hydrothermally altered rocks from the surface area of LHGF

An average χlf value of the basaltic rocks (1.93×10^{-6} m^3 kg^{-1}) from the surface of the LHGF (present study area) is lower than: (1) an average value of 65×10^{-6} m^3 kg^{-1} reported for the compiled basalts (Table 2) from the surface regions by Hunt et al. (1995) and (2) an average value of 22.9×10^{-6} m^3 kg^{-1} and 12×10^{-6} m^3 kg^{-1} reported, respectively, for the altered basalts from the geothermal wells KH1 and KH3 of the Krafla geothermal field by Oliva-Urcia et al. (2011). This shows that the basalt rocks from the surface area of LHGF are comparatively more altered than the basalts from the surface regions compiled by Hunt et al. (1995) as well as basalts from the geothermal wells KH1 and KH3 of the Krafla geothermal field (Table 2). Similarly, an average χlf value (1.97×10^{-6} m^3 kg^{-1}) of the rhyolites from the surface of the LHGF (present study area) is lower than the reported χlf value of 0–8.5×10^{-6} m^3 kg^{-1} for the altered rhyolites and dacites rocks from the surface of Acoculco geothermal field (AGF). This shows that the rhyolite rocks from the surface area of LHGF are also comparatively more altered than the rhyolites from the surface region of AGF. The abovementioned results may reveal that the nine andesite rocks are altered. It also confirms that χlf an easy to measure, reliable, and economical method that can be useful as an additional tool during the initial stage of exploration in the identification of altered rocks and zones of hydrothermal alteration in the geothermal areas.

Applicability of χlf versus χfd% in the identification of hydrothermally altered rocks from the surface area of LHGF

In the previous section, the applicability of χlf measurements and the binary diagram χlf versus χfd% in the identification of hydrothermally altered rocks in the 9 andesite rocks from LAGF was successfully validated. Now, these two methods are applied to 350 surface rocks from the LHGF to identify the fresh and altered rocks and zones of hydrothermal alteration. To avoid the lithological influence, the application of these two methods were separately applied for each rock type (basalts, rhyolites, trachyandesites, trachytes, and tuffs). A binary plot consisting of these two parameters (χlf versus χfd%), as presented by Dearing (1999), is used to differentiate fresh and altered rocks (Fig. 3). Based on this method, the rocks with χ_{fd}% values of < 3 and $\chi lf > 0.5 \times 10^{-6} m^3 kg^{-1}$ indicate that there are no SP grains, and the magnetic mineral assemblage is dominated by MD and SSD grains (Fig. 3 a) (Dearing et al. 1997). As the rocks with higher proportions of MD and SSD grains are indicative of relatively more altered, the rocks with χ_{fd}% values of < 3 and $\chi lf > 0.5 \times 10^{-6} m^3 kg^{-1}$ may indicate that they are relatively more altered.

To avoid lithological influence in the application of geochemical and rock magnetic parameters, we have applied these methods separately for each rock types, and the results are presented below.

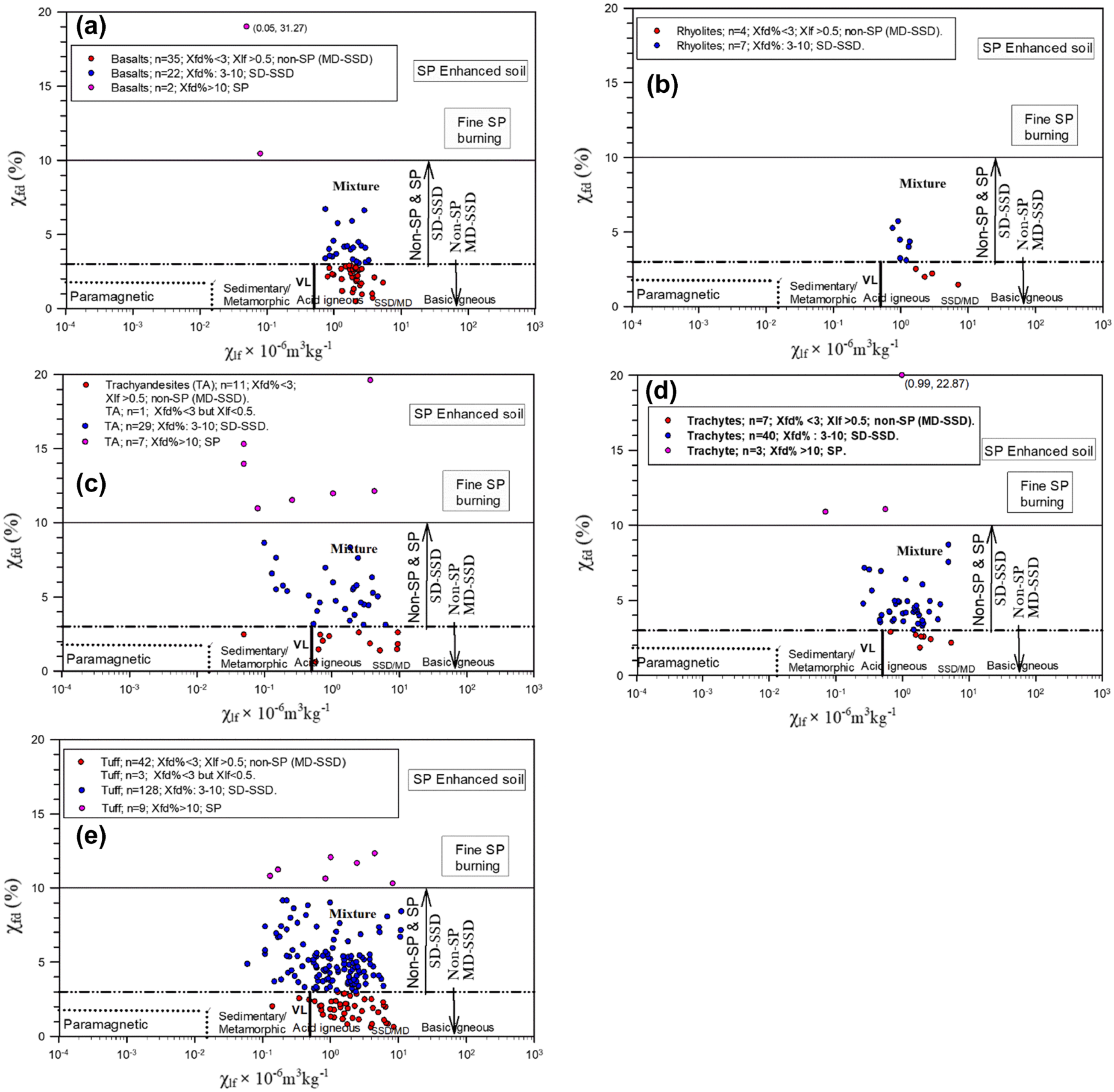


Fig. 3 Binary plots of magnetic susceptibility (χlf) values versus the percentage frequency dependent susceptibility (χfd%) for different rock types from the surface of Los Humeros geothermal field; **a** basalts, **b** rhyolites, **c** trachyandesites, **d** trachytes, and **e** tuffs

(a) Basalts (n = 59) χ_{lf} values of a total 59 basalt rocks vary between 0.05 and 5.39 ($\times 10^{-6}$ m^3 kg^{-1}) with a mean value of 1.93 ($\times 10^{-6}$ m^3 kg^{-1}), whereas χ_{fd}% of these rocks varies between 0.47 and 31.27 ($\times 10^{-6}$ m^3 kg^{-1}) with a mean value of 3.50 ($\times 10^{-6}$ m^3 kg^{-1}). These rocks are plotted in the binary plot of χ_{lf} vs. χ_{fd} % (Dearing et al. 1996; Fig. 3a). Dearing et al. (1996) have reported that the susceptibility is controlled by SSD or MD ferrimagnets in the samples where χfd% < 3 per cent and χlf > 0.5 × 10^{-6}m^{3}kg^{-1}. The samples in this plot are located as follows:

(i) Thirty-five rocks are occupied in the zone with χ_{fd} values of < 3% and χlf > 0.5 × 10^{-6}m^{3}kg^{-1} (Fig. 3 a), indicating that they are of altered basalt rocks.

(ii) Twenty-four rocks are in the zone with χ_{fd} values ranging between 3 and 10%. These rocks are considered as fresh or least-altered basalt rocks.

(b) Rhyolites (n = 11) χ_{lf} values of a total 11 rhyolite rocks varies between 0.76 and 7.18 (×10^{-6} m^3 kg^{-1}) with a mean value of 1.97 (×10^{-6} m^3 kg^{-1}), whereas $\chi_{fd\%}$ of these rocks varies between 1.44 and 5.71 (×10^{-6} m^3 kg^{-1}) with a mean value of 3.47 (×10^{-6} m^3 kg^{-1}). These rocks are plotted in the binary plot of χ_{lf} versus χ_{fd} % (Fig. 3b). The samples in this plot are located as follows:

- (i) Four rocks are located in the zone with χ_{fd} values of < 3% and χlf > 0.5 × $10^{-6}m^3kg^{-1}$ (Fig. 3 b), indicating that they are of altered rhyolite rocks.
- (ii) Seven rocks are located in the zone with χ_{fd}% values ranging between 3 and 10. These rocks are considered as fresh or least altered rhyolite rocks.

(c) Trachyandesite (n = 48) χ_{lf} values of a total 48 trachyandesite rocks varies between 0.05 and 9.48 (×10^{-6} m^3 kg^{-1}) with a mean value of 2.22 (×10^{-6} m^3 kg^{-1}), whereas χ_{fd} % of these rocks varies between 0.59 and 19.6 (×$10^{-6}m^3kg^{-1}$) with a mean value of 5.68 (×10^{-6} m^3 kg^{-1}). These rocks are plotted in the binary plot of χ_{lf} versus χ_{fd} and the samples in this plot are located as follows % (Fig. 3 c):

- (i) Eleven rocks are occupied in the zone with χ_{fd}% values of < 3 (Fig. 3 c) and χlf > 0.5 × $10^{-6}m^3kg^{-1}$ (Fig. 3 c); indicating that they are of altered trachyandesite rocks.

One rock sample (Ta-10) is located in the zone where χ_{fd}% values of < 3 (Fig. 3c) and the χlf value also < 0.5 × $10^{-6}m^3kg^{-1}$ (Fig. 3 c); below the dashed horizontal line at χ_{fd}% of 3 and left of the vertical line marked as VL. Due to this, the alteration status of this rock sample could not be identified.

- (ii) Twenty-nine rocks are located in the zone with χ_{fd}% values ranging between 3 and 10.
- (iii) Seven rocks are plotted in the zone with χ_{fd}% values of > 10. These rocks are considered as fresh or least-altered rhyolite rocks.

(d) Trachytes (n = 50) χ_{lf} values of a total 50 trachyte rocks varies between 0.07 and 5.47 (×10^{-6} m^3 kg^{-1}) with a mean value of 1.55 (×10^{-6} m^3 kg^{-1}), whereas $\chi_{fd\%}$ of these rocks varies between 1.83 and 22.87 (×10^{-6} m^3 kg^{-1}) with a mean value of 5.00 (×10^{-6} m^3 kg^{-1}). These rocks are plotted in the binary plot of χ_{lf} vs. χ_{fd} % (Fig. 3 d). The samples in this plot are located as follows:

- (i) Seven rocks are occupied in the zone with χ_{fd}% values of < 3 (Fig. 3d) and χlf > 0.5 × $10^{-6}m^3kg^{-1}$, indicating that they are of altered trachyte rocks.
- (ii) Forty rocks are located in the zone with χ_{fd}% values ranging between 3 and 10%; these rocks are considered as fresh or least-altered trachyte rocks.
- (iii) Three rocks are plotted in the zone with χ_{fd}% values of > 10. These rocks are considered as fresh or least-altered trachyte rocks.

(e) Tuffs (n = 182) χ_{lf} values of a total 182 tuff rocks varies between 0.02 and 11.05 (×10^{-6} m^3 kg^{-1}) with a mean value of 1.95 (×10^{-6} m^3 kg^{-1}), whereas $\chi_{fd\%}$ of these rocks varies between 0.59 and 32.52 (×10^{-6} m^3 kg^{-1}) with a mean value of 4.73 (×10^{-6} m^3 kg^{-1}). These rocks are plotted in the binary plot of χ_{lf} vs. χ_{fd} % (Fig. 3 e). The samples in this plot are located as follows:

- (i) Forty-two rock samples are occupied in the zone with χ_{fd}% values of < 3 (Fig. 3 e) and χlf > 0.5 × $10^{-6}m^3kg^{-1}$, indicating that they are of altered tuff rocks.

  Three rock sample (Tu-25, Tu-35, and Tu-40) is located below the dashed horizontal line at χ_{fd}% of 3 and left of the vertical line marked as VL, in the zone where χ_{lf} is < 0.5 (×10^{-6} m^3 kg^{-1}). Due to this, the alteration status of these three rock samples could not be identified.
- (ii) One hundred twenty-eight rocks are located in the zone with χ_{fd}% values ranging between 3 and 10, considered as fresh or least-altered tuff rocks.
- (iii) Nine rocks are plotted in the zone with χ_{fd}% values of > 10; these rocks are considered as fresh or least-altered tuff rocks.

Discussion

Nine intensively altered andesite rocks from the well Az-26 of the LAGF are selected for the application of the 3 geochemical and 2 rock magnetic methods. Recently, Pandarinath (2022) has reviewed the performances of 47 alteration indices and reported that CIA by Nesbitt and Young (1982) has very high success rate, and it is the topmost performer index. CIA values of all nine andesite rocks are > 60%; hence, these rocks are considered as altered rocks (Fig. 2 a). Similarly, the application of CIA for the chemical data of the fresh US Geological Survey standard reference materials AGV-2 (andesite) has provided a value of 45.7. This shows that CIA has indicated the correct value for this least-altered rock, because CIA value of < 60 considers it as a fresh rock whereas CIA value of > 60 sample for altered rocks.

LOI values of all 9 andesite rocks are very high, varying between 4.65 and 9.0%. The LOI values of these rocks are higher than the reported 1.85% for the fresh USGS standard reference rock AGV-2 (andesite; Lechler and Desilets 1987). Therefore, all 9 andesite rocks are considered as altered rocks (Fig. 2 b). The rock samples with > 2% of H_2O^+ may be considered as altered rocks (Le Bas et al. 1986). Though strictly H_2O^+ is not equal to LOI, the rocks reported with the values of LOI or H_2O^+ > 2% may be considered as altered rocks.

The third geochemical method is the binary plot which is represented by major element composition of the felsic mineral component ($CaO + K_2O + Na_2O$) on the X-axis and those representing mafic mineral component ($Fe_2O_3^T + MnO + MgO$), representing the Y-axis (for more details of the plot, see the above results section). The 9 andesite rocks whose alteration status is being identified in this work plotted as a group (marked as Gr-2 in the Fig. 2 d) towards origin of the plot and almost equidistance to the X-axis and Y-axis, which indicates that the andesite rocks are altered rocks and their chemical composition is intermediate (neither felsic nor mafic). As the rocks with known alteration status have plotted in correct locations (Fig. 2 d) in the map, the 9 andesites may be considered as altered rocks with an intermediate composition.

The application of the rock magnetic methods in identification of alteration in the rocks has revealed that χlf values of the 9 andesite rocks varies between 0.37 and 11.2×10^{-6} m^3 kg^{-1} (Pandarinath et al. 2014, 2019). These χlf values are comparable to the reported χlf values ranges from 0.12 to 11.58×10^{-6} m^3 kg^{-1} for the altered andesites from the surface to bottom (0–2360 m depth) in the well Az-49 of the LAGF (Table 2). However, χlf values of the 9 andesite rocks are much lower than the average χlf values reported for the surface andesite rocks reported in the literature ranges between 0.08 to $61 \times 10^{-6} m^3 kg^{-1}$ (Hunt et al.1995). An average χlf values of andesite rocks reported in the literature varies between 0 and 61×10^{-6} m^3 kg^{-1}. There are some works in the literature (Lapointe et al. 1986; Harding et al. 1988; Xu et al. 2003; Just et al. 2004) where an average lower

Table 2 Comparison of χlf and the status of hydrothermal alteration in the surface rocks of different rock formations from geothermal and volcanic systems

Geothermal field	Drilled well/surface	Rock type	Samples (n)	Av. Mag. Sus χlf (10^{-6} m^3 kg^{-1})	Altered/fresh	Reference
Los Humeros GF, Mexico	Surface	Basalts	59	1.93	Fresh/altered	This work
Krafla geothermal field, Iceland	Well KH1	Basalts	9	0.23	Altered	1
	Well KH3	Basalts	47	0.12	Altered	1
Average (Hunt et al. 1995)	Surface	Basalts	-	65	-	2
Ijen Volcanic Complex, Indonesia	Surface (Lava)	Basalts	-	14.71	Fresh	3
		Basalts, BA, and BTA	-	7.35–17.95	Fresh	3
Los Humeros GF, Mexico	Surface	Rhyolites	11	1.97	Fresh/altered	This work
Los Azufres GF, Mexico	Well Az-26 0–460 m depth	Rhyolites and Rhyodacites	12	0.13–2.26	Altered	4
Acoculco GF Mexico	Surface	Acid rocks (rhyolites and dacites)	38	0–8.5	Altered (intense)	5
Average (Hunt et al. 1995)	Surface	Rhyolites	-	0.1–15	-	2
Los Humeros GF, Mexico	Surface	Trachyandesites	48	2.22	Fresh/altered	This work
Los Azufres GF, Mexico	Well Az-26 460–1200 m depth	Andesites	19	0.28–9.16	Altered (intense)	5
Los Azufres GF, Mexico	Well Az-49 0–2360 m depth	Andesites	61	0.12–11.58	Altered (intense)	5
Average (Hunt et al. 1995)	Surface	Andesites	-	0.084–61	-	2
Los Humeros GF, Mexico	Surface	Trachytes	50	1.55	Fresh/altered	This work
Los Humeros GF, Mexico	Surface	Tuffs	182	1.95	Fresh/altered	This work
North Sumatera Province, Sumatra	Surface	Toba Tuff	-	1.198	-	6
Igneous rocks (average)	Surface	Igneous rocks	-	1–100	Fresh	2
Acidic igneous rocks (average)	Surface	Acidic igneous rocks	-	0.014–13	Fresh	2
Basic igneous rocks (average)	Surface	Basic igneous rocks	-	0.2–44	Fresh	2

1, Oliva-Urcia et al. (2011); 2, Hunt et al. (1995); 3, Pratama et al. (2018); 4, Pandarinath et al. (2014); 5, Pandarinath et al. (2020); 6, Siregar et al. (2022)

χlf values (0.12–0.23 × 10^{-6} m^3 kg^{-1}) are observed for rocks affected by high intensity of alteration (Table 2). In these cases, it is reported that alteration lowers the magnetic susceptibility of the rocks, because of a lowered magnetite and/or other Fe-bearing minerals in the altered rocks. The basaltic rocks from two geothermal wells KH1 and KH3 from the Krafla geothermal field, Iceland, have shown an average χlf values value of 22.9 average a 10^{-6} m^3 kg^{-1}) suggesting a destruction of magnetic minerals by hydrothermal activity. The main alteration processes in such an environment is the fluid-rock interactions. Therefore, low susceptibility samples were surely modified by hydrothermal processes; however, the very beginning of hydrothermal alteration cannot not be traced using only this criterion. Magnetic susceptibility can be a useful parameter, during the initial stages of geothermal exploration, in identifying hydrothermally altered rocks and zones of hydrothermal alteration both at the surface and from drilled wells in geothermal systems.

Generally, SP particles are smallest grains (highest χlf values), SSD particles are smaller grains (medium χlf values), and MD magnetic particles are largest grains (lowest χlf values). This indicate that MD grains (lowest susceptibility), SSD grains (medium level susceptibility), and SP grains (highest susceptibility) represent higher, moderate, and least alterations, respectively. χlf values are lower for rocks with a high intensity of alteration (Xu et al. 2003). Hence, it can be understood that the hydrothermally altered rocks are characterized by SSD particles (sometimes MD). Dearing et al. (1996) has suggested that the susceptibility is controlled by SSD or MD ferrimagnets in the samples where χfd% < 3% and χlf > 0.5 × $10^{-6}m^3kg^{-1}$.

Application of the χlf for differentiating fresh and altered rocks from the surface area of LHGF

χlf is extensively being applied for identification of hydrothermal alteration of primary magnetic minerals (with high χlf values) to secondary minerals (with low χlf values). χlf along with other rock magnetic parameters, for example, χfd%, will be comparatively more effective in their application. χlf values are measured for the surface basalt rocks (n = 59; 1.93 × $10^{-6}m^3kg^{-1}$) and those of rhyolite rocks (n = 11; 1.97 × $10^{-6}m^3kg^{-1}$) from LHGF. These measured values are lower than the average χlf values of the surface basic igneous rocks (0.2–44 × $10^{-6}m^3kg^{-1}$) and acidic (0.01–13 × $10^{-6}m^3kg^{-1}$) igneous rocks compiled and reported by Hunt et al. (1995; Table 2).

Application of the binary plot (χlf vs. χfd%) in differentiating fresh and altered rocks from the surface area of LHGF

χlf and χhf are measured for all 350 surface rock samples from LHGF. Based on these parameters, along with that compiled from the literature for several rocks from the geothermal fields, (Table 2) the following observations are mentioned.

The number of surface rocks of LHGF characterized by χfd% values of < 3 × 10^{-6} m^3 kg^{-1} and χlf > 0.5 × $10^{-6}m^3kg^{-1}$ (Fig. 3) are (1) 35 out of 59 basalts (59.3%); (2) 4 out of 11 rhyolites (36.4%); (3) 11 out of 48 trachyandesite (22.9%); (4) 7 out of 50 trachytes (14%); and (5) 42 out of 182 tuffs (23.1%). This indicates that 99 out of a total 350 rocks (all rock types together) are altered rocks (28.3%) and the remaining 251 rocks (71.7%) are least altered or fresh rocks. Apart from these rocks, one trachyandesite (Ta-10) and three tuff samples (Tu-25, Tu-37, and Tu-40) are having χlf < 0.5 × $10^{-6}m^3kg^{-1}$, and hence, these four rocks are not classified.

Mapping of the zones of hydrothermal alteration

The rock samples identified as fresh and altered are based on χlf and the binary plot (χlf vs. χfd%) where it is shown that the altered rocks are characterized by χ_{fd}% values of < 3 (Fig. 3 a) and χlf > 0.5 × $10^{-6}m^3kg^{-1}$. Based on this method, 99 out of a total 350 surface rocks at LHGF are identified as altered rocks. The distribution of the altered rock samples identified based on the rock magnetic parameters, in the study area, clearly indicates two major hydrothermally altered zones in the study area. Zone 1 is in the southern part of the caldera (marked the boundary with dashed line; marked as Zone 1; Fig. 1) where 23 out of the total 35 rock samples (62.9%) are identified as altered rocks. The Zone 2 is in the northern part of the caldera (marked the boundary with dashed line; marked as Zone 2; Fig. 1) where 23 out of 27 rocks (85%) were identified as altered rocks. Investigating the possible agents responsible for the hydrothermal alteration has led us to the fault systems, which are controlling the hydrothermal alteration in the surface area of the LHGF. Superimposing the locations of the rocks on a geological and tectonic map of the study area has indicated that more altered rocks are located very near to the faults in the region (Fig. 1).

Results obtained by rock magnetic parameters are comparable to those reported in the literature, which also reveals that there are number of faults crosses the main production zone of the LHGF and these faults are responsible for secondary permeability in the reservoir (Toledo et al. 2020). There are several faults in the study area surrounding which the altered rocks are located (Fig. 1). Some faults (e.g., Los Humeros fault and the Loma Blanca fault) favor fluid flow and present strong hydrothermal alteration at the surface (Norini et al. 2015, 2019; Toledo et al. 2020). The faults Los Humeros, Maxtaloyat, Loma Blanca, and several other faults permit fluid flow and present strong hydrothermal alteration at the surface (Norini et al. 2015, 2019). However, the present study shows that there are not many altered rocks on the surface region between the Las Papas and Las Viboras faults (Fig. 1). This is in accordance with the reported hidden faults at LHGF (Izquierdo et al. 2000) based on subsurface geology and petrological and geophysical logs. Norini et al. (2019) have reported that there is a deeper fluid pathway toward the east and due to this the area between and surrounding the Las Papas and Las Viboras faults show no hydrothermal alteration along their strike at the surface. This is reflected in the absence of any altered rocks in this area (Fig. 1). This suggests that the presence or absence of surface hydrothermal alteration at LHGF is mainly controlled by the faults.

Conclusions

Based on the geochemical and rock magnetic studies on hydrothermal alteration in the surface rocks from Los Humeros geothermal field, the following conclusions are made:

- The applicability of some of the geochemical and rock magnetic methods in identification of hydrothermally altered rocks and zones of alteration is successfully validated.
- χlf values are lower for rocks with a high intensity of alteration.
- Hydrothermally altered rocks are characterized by SSD-MD particles.
- χlf and the binary plot (χlf vs. χfd%) methods have identified 99 out of a total 350 surface rocks at LHGF are as altered rocks.
- The distribution of the altered rock samples identified based on the rock magnetic parameters, in the study area, clearly indicates two major hydrothermally altered zones; Zone 1 is in the southern part of the caldera and in the Zone 2 is in the northern part of the caldera.
- Hydrothermally altered rocks on the surface of the LHGF are, in general, associated with the surface faults systems. However, altered rocks are not observed along and surroundings of some of the faults at the surface (e.g., area between the Las Papas and Las Viboras faults) because these faults exhibit only a deeper fluid pathway.
- Finally, it may be confirmed that χlf and χfd% are easy to measure, reliable, and economical methods which can be useful as an additional tools during the initial stage of exploration in the identification of altered rocks and zones of hydrothermal alteration in the geothermal areas.

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Data availability The data used in this article is available from the corresponding author (pk@ier.unam.mx).

Declarations

Conflict of interest The authors declare no competing interests.

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