Geology and geochemistry of jasperoids from the ‘Montaña de Manganeso’ district, San Luis Potosí, north-central Mexico

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ABSTRACT

Large outcrops of jasperoids occur in the ‘Montaña de Manganeso’ mining district in north-central Mexico. They range from massive manganiferous jasperoids to highly brecciated, hematitic jasperoid. The jasperoids of ‘Montaña de Manganeso’ occur mainly as replacements of limestone, sandstone and shale, commonly nearby high-angle fault systems. The mineralogy of the jasperoids consist of quartz and its polymorphs (chalcedony, tridymite and cristobalite), Fe-Mn oxy-hydroxides, calcite and minor barite. Many outcrops show evidence of several periods of brecciation and silicification. The geochemical signature of the jasperoids suggests that silicification was product of hydrothermal activity. The jasperoids display enrichment in elements of hydrothermal provenance such as Ba, Sr, As, Cr, Mo, Sb, Ni, Zn and Cu, whereas are strongly depleted in the elements indicative of clastic sources such as Ti, K, Th and Zr. Element ratios such as (Fe+Mn)/Ti, Al/(Al+Fe+Mn), Fe/Mn and U/Th, along with the ternary diagrams confirm a hydrothermal origin. A low ∑REE, enrichment of LREE over HREE, negative Ce anomalies and positive Y anomalies (Y PASS/HoPAAS) also support the hydrothermal processes. The geological evidence, in the form of a feeder zone and extensive hydrothermal alteration, show that the silica forming the rocks originated from ascending hot fluids.

Key words: jasperoid; hydrothermal; silicification; Fe-Mn oxides; San Luis Potosí.

RESUMEN

En el distrito minero de la Montaña de Manganeso en el centro-norte de México se encuentran grandes afloramientos de jasperoides que van desde jasperoides manganíferos masivos hasta jasperoides hematíticos muy brechados. Los jasperoides de la Montaña de Manganeso ocurren principalmente como reemplazamientos de calizas, areniscas y pizarras, comúnmente cerca de sistemas de fallas de alto ángulo. La mineralogía de los jasperoides consiste en cuarzo y sus polimorfos (calcedonia, tridímita y cristobalita), oxihidróxidos de Fe-Mn, calcita y en menor grado barita. Muchos afloramientos muestran evidencia de varios episodios de brechamiento y silicificación. La firma geoquímica de los jasperoides sugiere que la silicificación fue producto de la actividad hidrotermal. Los jasperoides muestran enriquecimiento en elementos de procedencia hidrotermal como Ba, Sr, As, Cr, Mo, Sb, Ni, Zn y Cu, mientras que están fuertemente empobrecidos en los elementos indicativos de fuentes clásicas como Ti, K, Th y Zr. Relaciones de elementos como (Fe+Mn)/Ti, Al/(Al+Fe+Mn), Fe/Mn y U/Th, junto con las diagramas ternarios Al-Fe-Mn y Fe-Mn- (Ni+Co+Cu)×10 confirman un origen hidrotermal. Un bajo ∑REE, un enriquecimiento de LREE sobre HREE, anomalías negativas de Ce y positivas de Y (Y PASS/HoPAAS) también apoyan un origen hidrotermal. La evidencia geológica, en forma de una ‘zona de alimentación’ y alteración hidrotermal extensa, muestra que la sílice que forma las rocas se originó a partir de fluidos calientes ascendentes.

Palabras clave: jasperoide; hidrotermal; silicificación; óxidos de Fe-Mn; San Luis Potosí.

INTRODUCTION

Jasperoid is a rock composed mainly of quartz and/or other silica polymorphs, formed by epigenetic hydrothermal replacement of a previously lithified rock (Lovering, 1962, 1972; Fournier, 1985; Theodore and Jones, 1992; Hofstra and Clíne, 2000; Yigit et al., 2006). They are documented in several countries including the United States, Mexico, Peru, Australia and China, where they form topographically prominent outcrops because of their resistance to weathering (Bailey, 1974; Murphy, 1995; Arehart, 1996). Lovering (1972) investigated several jasperoid provinces and districts in the USA and Mexico recognizing a genetic and spatial association between jasperoid and ore deposits.
Jasperoid formation is commonly attributed to hydrothermal activity because of a general spatial relationship between jasperoids and igneous rocks (Lovering, 1972; O’Neil and Bailey, 1979; Wilson et al., 1987; Nelson, 1990; Theodore and Jones, 1992; Murphy, 1995; Johnston et al., 2008; Kirwin and Royle, 2019; Huff et al., 2020). Consequently, most jasperoids are localized along faults, fractures, and shear zones that could serve as channel ways for ascending silicic-rich hydrothermal fluids (McKay and Finlow-Bates, 1977; Wilson et al., 1987; Kuehn and Rose, 1992; Yigit et al., 2006). Some jasperoids, however, form lenticular and layered bodies that may resemble bedded chert (Lovering, 1972). Such jasperoids may be difficult to distinguish from bedded cherts, unless the feeder channels can be identified (Lovering, 1972; Wilson et al., 1987; Nelson, 1990).

Jasperoid deposits, as hydrothermal products, can be expected to exhibit the geochemical signature of the fluids from which they precipitated (Renault et al., 1995). Moreover, as jasperoids generally contain substantial amounts of Fe and Mn oxides with strong adsorption capacity for cations, they even more strongly acquire the geochemical signatures of the mineralizing fluid (Bau et al., 1996; Conly et al., 2011; Sinisi et al., 2012; Papavassiliou et al., 2017). Also, as they are very resistant to chemical weathering and are barely affected by diagenetic changes, their chemistry is suitable for interpreting depositional processes and environment of formation of associated ore deposits (Murray, 1994; Dasgupta et al., 1999). For this reason, jasperoids and their geochemistry have long been applied to mineral exploration, in particular, gold exploration (Lovering and Heyl, 1974; O’Neil and Bailey, 1979; Holland et al., 1988; Nelson, 1990; Graney et al., 1991; Theodore and Jones, 1992; Kirwin and Royle, 2019; Huff et al., 2020).

Massive siliceous bodies crop out prominently in the Central Plateau region of Mexico (Labarthe-Hernandez et al., 1992). These bodies occur as fault-controlled veins and irregular bodies that cut rocks of known continental origin, making it unlikely that they are submarine exhalative Fe-Mn cherts (Crerar et al., 1982; Adachi et al., 1986). Hence, in agreement with previous studies involving these bodies (Albinson, 1988; Labarthe-Hernández et al., 1992), the term jasperoid is preferred here for the Central Plateau siliceous bodies to avoid connotation of diagenetic or exhalative origin usually associated with the term chert (Adachi et al., 1986; Murray, 1994; Murphy, 1995; Binns, 2007).

The common association of jasperoids with precious and base-metal enrichment has focused attention on these metals and not on their generally sub-economic iron and manganese content (Hesse, 1990). This investigation instead takes advantage of the high abundances of manganese and iron oxides in the jasperoids of the Central Plateau region to characterize and understand jasperoid formation through the Fe-Mn oxide geochemistry. The problem of differentiating hydrothermal silica from other types such as biogenic and sedimentary silica is dealt with by demonstrating through field and geochemical characteristics of the jasperoids, the hydrothermal origin of both the silica and the Fe-Mn oxides. The results of this research provide a new approach to understand the metallogenesis of the Central Plateau.

REGIONAL GEOLOGY

The study area is located in central Mexico on an elevated plateau (average altitude: ~2000 m a.s.l.) known as the Mesa Central or Central Plateau (Figure 1) (Nieto-Samaniego et al., 2005, 2019). The geology of the study region is characterized by the accretion of the Guerrero terrane over continental Mexico represented by the Sierra Madre terrane (Centeno-Garcia and Silva-Romo, 1997; Centeno-Garcia et al., 2003; Martini et al., 2013). Jurassic ocean floor and island arc volcanic-sedimentary rocks geologically circumscribed to the Guerrero terrane accreted over the Sierra Madre terrane marine carbonate successions during the Late Cretaceous Laramide orogenesis (Centeno-Garcia and Silva-Romo, 1997; Centeno-Garcia et al., 2003; Martini et al., 2013). In the region, isolated outcrops of intraoceanic arc andesitic and pillow lavas, cherty pelagic limestones and radiolarite-chert blocks
characterize the Guerrero terrane (Centeno-García and Silva-Romo, 1997) (Figure 2).

Marine Mesozoic successions of late Triassic to late Cretaceous age constitute the Sierra Madre terrane (Carrillo-Bravo, 1982; Juárez-Arriaga et al., 2019). The basement rocks, which correspond to Upper Triassic-middle Jurassic turbidites (Centeno-García and Silva-Romo, 1997; Barboza-Gudiño et al., 1998, 2010), are overlain by Lower to Middle Jurassic continental arc deposits (Barboza-Gudiño et al., 1999, 2008). Upper Jurassic to Late Cretaceous shallow marine carbonate sequences and clastic sediments cover the continental arc deposits (Carrillo-Bravo, 1982).

The Guerrero terrane accretion to continental Mexico in the Late Cretaceous, caused by the subduction of the Farallon plate beneath the North American plate, produced regional thrust faults (Figure 2). These faults were partly reactivated as normal faults during the subsequent development of the Paleogene Basin and Range extensional tectonics (Tristán-González et al., 2009b). The transition from compressional tectonics of the Guerrero terrane accretion to extensional tectonics of the Basin and Range was marked by the onset of the continental volcanism of the Sierra Madre Occidental (Ferrari et al., 2002; Aguirre-Díaz et al., 2008). During the Oligocene, the ignimbrite flare-up event resulted in the large-volume ignimbrites which make the Sierra Madre Occidental one of the largest silicic igneous province on earth (Mcdowell and Clabaugh, 1979; Ferrari et al., 2002, 2007; Aguirre-Díaz et al., 2008; Aguirre-Díaz and Labarthe-Hernández, 2003).

The partial overlap of this silicic magmatic event and the Basin and Range extension generated multiple and discrete episodes of fissural rhyolitic volcanism mostly controlled by major NW–SE trending fault systems (Tristán-González, 1986; Aguirre-Díaz and Labarthe-Hernández, 2003; Aguirre-Díaz et al., 2008; Tristán-González et al., 2008, 2009b; Aguilón-Robles et al., 2012, 2014; Zamora-Vega et al., 2018). The silicic nature of the volcanism also ensured the supply of vast amounts of silica, which generated extensive areas of jasperoid occurrences in the Central Plateau (Labarthe-Hernández et al., 1992). The Sierra Madre Occidental magmatism triggered a period of intense hydrothermal activity in the Central Plateau that generated different types of mineral deposits (Aranda-Gómez and Mcdowell, 1998; Aranda-Gómez et al., 2007; Nieto-Samaniego et al., 2007; Tristán-González et al., 2008, 2009b; Rodríguez-Ríos et al., 2013). In the Zacatecas state, west of the study area, this hydrothermal activity is associated with precious metal and polymetallic epithermal deposits (Ponce and Clark, 1988; Henry and Aranda-Gómez, 1992; Nieto-Samaniego et al., 1996, 2007; Aguirre-Díaz et al., 2008; Aguilón-Robles et al., 2009; Zamora-Vega et al., 2018).

**METHODOLOGY**

Eleven highly silicified samples, collected from different outcrops, were analyzed for this study. Most of these are jasperoids, but three of the samples show contents of silica (<10.1 %) lower than those of jasperoids (Lovering, 1972) due to high contents of MnO₂, and in fact represent manganese ore. However, for convenience, the general term jasperoid is used here for all the samples analyzed.

Textural characterization of the Fe–Mn oxides was first carried out visually in hand specimens and in thin sections. For a more detailed textural and mineral identification, petrography and scanning electron microscopy (SEM) were carried out on six polished sections at the Central Analytical Facility of the Faculty of Science of the University of Johannesburg, South Africa. Energy dispersive spectrometry (EDS) was used for semi-quantitative determination of concentration of elements in certain minerals. Microscopic images were taken on carbon-coated polished sections using backscattered electrons (BSE) on a Vega 3 Tescan system equipped with an Oxford X-Max 50 mm² energy dispersive spectrometer (EDS). The software used was an Oxford Aztec software V. 2.2.

Figure 2. Generalized geologic map of the study area (modified after SGM, 2001).
Bulk mineralogy of 10 samples was determined by powder X-ray diffraction (XRD) using an Empyrean diffractometer equipped with Ni filter, a Cu tube of fine focus and a PIXcel3D detector, at the Instituto de Geología, Universidad Nacional Autónoma de México (UNAM). Measurements were performed in the 2θ angular range from 5° to 70°, in step scanning with a step scan of 0.003° (2θ) and an integration time of 40 s per step. Rock samples were previously crushed and milled to 200 mesh and homogenized. Data were interpreted using HighScore Plus v4 software (PANalytical). Conventional search and match techniques were employed for qualitative analysis.

Major and trace elements (including REE) concentrations were determined for nine samples at Activation Laboratories (ActLabs, Canada) using the Lithogeochemistry analytical package ‘4Litho’. This method is a combination of lithium metaborate/tetraborate fusion ICP whole rock for major elements and ICP-MS for major elements and REE (for details see http://www.actlabs.com). Calibration was performed using prepared USGS- and CANMET-certified reference materials. A correlation matrix of elemental concentrations was prepared using the software Statistica version 13. Binary and ternary discrimination diagrams were processed with the GCDkit package for R version 3.6.0.

To evaluate the influence of hydrothermal activity, the Fe/Mn (Hein et al., 1997), (Fe+Mn)/Ti (Jun et al., 2010) and Al/(Al+Fe+Mn) ratios were calculated (Adachi et al., 1986). To determine the source of Fe and Mn in the jasperoids Ce and Eu anomalies (Ce/Ce* and Eu/Eu*) were calculated using the equations proposed by Taylor and McLennan (1985):

\[
\text{Ce/Ce*} = (\text{CeCN} \sqrt{[(\text{LaCN})(\text{PrCN})]})
\]

\[
\text{Eu/Eu*} = (\text{EuCN} \sqrt{[(\text{SmCN})(\text{GdCN})]})
\]

wherein these expressions, Eu and Ce are the actual concentrations and Eu* and Ce* are the predicted concentrations based on interpolation of neighboring REE, using chondrite-normalized abundances (Boynton, 1984). The Y anomaly, also used to determine the source of Fe and Mn, was calculated using the equation \(\text{Y}_{\text{PAAS}}/\text{Ho}_{\text{PAAS}}\) (Bau et al., 2014). The subscript “CN” and “PAAS” indicate chondrite-normalized (Boynton, 1984) and Post Archean Australian Shale normalized values, respectively. The heavy-REE (HREE), middle-REE (MREE) and light-REE (LREE) are defined as the elements from La to Nd, Sm to Tb and Dy to Lu, respectively.

**GENERAL CHARACTERISTICS OF MEXICAN JASPEROIDS**

Several protruding jasperoid outcrops (Figure 1) are documented in the Mexican Central Plateau (Labarthe-Hernández et al., 1992). The jasperoids generally occur as flared-up, funnel shaped veins of widely variable dimensions. Tabular bodies with thicknesses ranging from 2 to 20 m (and rare bodies of up to 50 m) occur occasionally, extending up to 2 km in length (Labarthe-Hernández et al., 1992). Most jasperoid bodies are black or red, although yellow-green, brown and green colored jasperoids are also present. Outcrops range from hard, massive jasperoids to highly brecciated jasperoids re-cemented by younger quartz. Textures vary from aphanitic to coarse crystalline varieties. Late quartz, calcite and barite form crosscutting veinlets or fill vugs and open spaces (Labarthe-Hernández and Aguilón-Robles, 1986). Iron and manganese oxides dominate the non-silica components of the jasperoids.

Most jasperoid bodies trend NW-SE (with subordinate NE-SW and E-W directions) and are fracture controlled (Labarthe-Hernández et al., 1992). The NW-SE trending direction fairly coincides with that of the regional San Luis-Tepehuanes-fault system, whose main activity occurred during the early Oligocene, with multiple reactivations in the late Oligocene and Miocene (Nieto-Samaniego et al., 2007). This fault system controlled the distribution of several mineral deposits in the Central Plateau (Camprubi and Albinson, 2007; Nieto-Samaniego et al., 2007). The manganiferous jasperoids are more widespread in the regions close to the boundary of the Guerrero terrane and the Sierra Madre terrane, where they constitute a metallogenetic belt (Labarthe-Hernández et al., 1992; Sánchez-Rojas, 2013). Trask and Rodríguez-Cabo (1948) reported at least 20 manganiferous jasperoids in this region, with exploitation of the manganese content occurring at Montaña de Manganeso (MdM) and the La Abundancia districts (~60 km W of MdM). A similar close spatial relationship exists between jasperoids and base metal deposits at Real de Ángeles and Villa de Ramos (~55 and 100 km SSE of MdM, respectively) (Labarthe-Hernández et al., 1992).

The jasperoids of the Central Plateau replace Cretaceous marine carbonate rocks of the Sierra Madre terrane, but occasionally replace volcano-sedimentary rocks of the Guerrero terrane and Oligocene continental igneous rocks (Labarthe-Hernández et al., 1982, 1992). Silicification is typically pervasive, obliterating the original characteristics of the rocks. However, in some jasperoids the replacement is partial, preserving the original host rock textures. An argillic alteration often occurs laterally to the jasperoids suggesting formation from near neutral pH, low temperature hydrothermal solutions (cf. Reyes, 1990; Sánchez-Córdova et al., 2019; Fulignati, 2020). According to Labarthe-Hernández and Aguilón-Robles (1986), the jasperoids formed from replacement of host rocks by multiple silica generations ejected from ascending hot fluids during the waning stage of hydrothermal activity associated with mostly unidentified intrusions.

The age of the Central Plateau jasperoids is not well constrained. The available ages, based on stratigraphic correlation of replaced rocks and the age of the associated intrusives, are not consistent, varying from <30 Ma to >32.7 Ma (K/Ar) (Labarthe-Hernández et al., 1992). Based on intimate spatial association to intrusive rocks of Tertiary age, the jasperoids assumed the age of the associated intrusives to be Oligocene. This age is consistent with the 30 to 35 Ma (K/Ar) range estimated for the La Colorada, Fresnillo and Sombrerete jasperoids (Albinson, 1988).

**The Montaña de Manganeso jasperoids**

Jasperoids from the MdM occur primarily as fault-controlled blocky bodies of variable size (Figure 3a, 3b), mostly confined to NE- trending faults within strongly folded and fractured volcaniclastic rocks (Trask and Rodríguez-Cabo, 1948; Wilson and Rocha, 1948; Alexandri, 1976). The epigenetic nature of the jasperoids is unambiguous, exhibiting a cross-cutting relationship with their host rocks. The jasperoids generally strike N 25° E with a dip of 70° to 80° NW (Wilson and Rocha, 1948). Occasionally they present transitional contacts that grade into partly silicified limestone, sandstone and shale. They are closely associated with manganese ores, and occasionally present mutual cutting relationships and gradational contacts.

In MdM red and black jasperoids usually occur spatially separated (Figure 3a, 3b). However, occasionally the hematitic (red) jasperoids gradually change into the manganiferous (black) jasperoids, which in turn transition into Mn ore with an associated increase in Mn content (Figure 4).

The differences in color reflect varying proportions of non-silica minerals, particularly the iron and manganese oxide content (Figure 3c, 3e, 3f). The red jasperoids are rich in iron oxides, mainly hematite, which imparts them a distinctive intense red tint (Figure 5a–5d). Minor yellowish brown (goethitic) and rare green (pyritiferous) varieties also occur among the Fe rich jasperoids (Figure 5e–5g). Some jasperoids are mineralogically heterogeneous, with cm to mm scale variations in color visible at outcrop and thin section scale (Figure 3d). Bleaching of...
the hematitic jasperoids produced a characteristic pseudo-brecciated texture characterized by hematite-rich zones surrounded by a white microcrystalline matrix (Figure 5b). The manganiferous jasperoids are less heterogenous, exhibiting various shades of gray (Figure 5i–5l) depending on the Mn oxide concentrations.

The MdM jasperoids display a variety of macroscopic textures such as massive (Figures 3a, 3b, 5e), brecciated (Figure 5a–5c) and laminated (Figure 6a, 6b). These textures are a result of multiple episodes of replacement, brecciation, and veining through episodic injection of silica by the hydrothermal system. Massive jasperoids are relatively common and have a dense aphanitic texture that reflects uniform distribution of either manganese oxides (Figure 7c) or hematite grains (Figure 7d, 7h) within the silica matrix. The laminated jasperoids consist of fine grained visually distinctive hematite-rich laminae variably modified or obliterated by veining and brecciation (Figures 6c-6f, 7a, 7b). Veining is manifested as a network of quartz veinlets that replace older generations of quartz and Fe-Mn oxides (Figure 8f, 8g). Brecciation is characteristic of samples from the feeder zone (Figure 3g).

The jasperoids also exhibit several ductile (Figure 6a, 6b) and brittle (Figure 6d, 6f) deformation structures. Diagenetic dehydration (Figure 6c, 6e) produced fractures expressed as a pseudobreccia texture in some jasperoids. These structures are easily identifiable in the red iron-rich jasperoids but are less visible in the black manganese-rich jasperoids because the darker color of the latter has obscured them (Figure 6i-6l).

RESULTS

Petrography

Quartz, the main component of the jasperoids at MdM, occurs mainly as anhedral crystals ranging in size from cryptocrystalline to microcrystalline and coarse crystalline (<2 mm) (Figure 8a–8c). A greater part of the quartz appears to have recrystallized fromchalcedony (Figure 5k), as in most samples a transition from chalcedony to coarse quartz is observed (Figure 8d, 8e). Rare euhedral quartz grains (Figure 8h, 8i), probably representing quartz precipitated directly from the hydrothermal fluid, also occur. Late stage quartz appears as mostly anhedral coarse crystalline grains that fill fractures whose walls are lined by a thin layer of microcrystalline quartz (Figures 5j, 8f, 8g).

Manganese and iron oxides are ubiquitous in the jasperoids. They mostly occur as Fe-oxide rich and Mn-oxide rich bands (Figure 7a, 7b). The intense black, red or brown colored jasperoids suggestive of high Fe-Mn oxide contents can actually result from silica sparsely stained with disseminated and fine-grained manganese oxides (Figure 7c),

Figure 3. Representative outcrop photos of jasperoids from the Montaña de Manganeso: (a) Blocky hematitic jasperoids. (b) Manganiferous jasperoids with calcite veins. (c-f) Veined and mineralogically heterogeneous jasperoids, with mm to cm scale variations in color visible at outcrop scale; a complete separation of Mn and Fe in the jasperoids is commonly observed. (g) Exposed part of the feeder zone with silicified Fe-Mn oxides lining the fractures.

Figure 4. Schematic cross-section of an ore related jasperoid body at Montaña de Manganeso showing major alteration and mineralization features. The ore occur as massive black lenses of manganiferous jasperoids within hematitic jasperoids. The jasperoids have associated zones of argillic alteration that are suggestive of a hydrothermal origin.
Fe, Mn and volatile components (LOI) (Table 2). SiO₂ concentrations in the jasperoids vary from 65.53 to 91.96 wt.% in the non-ore jasperoid proper. The high values of SiO₂ reflect the abundance of quartz and its polymorphs tridymite, cristobalite and chalcedony, as the dominant minerals in the jasperoids.

The MnO(tot) varies from 0.08 to 12.44 wt.% in the jasperoids proper, and from 57.68 to 59.69 wt.% in the two ore samples analyzed here. High Mn concentrations are related to the occurrence of Mn oxides (birnessite, todorokite and hollandite; Table 1). Fe₂O₃(tot) content in the jasperoids varies from 1.31 to 32.09 wt.%, related with the presence of hematite and subordinate goethite, magnetite and pyrite. In the two ore samples Fe₂O₃(tot) concentrations are low, ranging from 1.31 to 2.77 wt.%. The Al/(Al+Fe+Mn) ratio for the MdM jasperoids varies from 0.01 to 0.05, with one anomalous value of 0.45. The ratios (Fe+Mn)/Ti and Fe/Mn vary widely, from 76 to 94803 and from 0.02 to 152.95, respectively.

The remaining major elements (Ti, Al, Mg, Ca, Na, K, and P) are less than 3 wt.%. CaO (<1.46 wt.%) concentrations can be accounted for by the presence of calcite and/or the Ca content in the lattice structure of some manganese oxides such as todorokite and birnessite. The low concentrations of K₂O (<0.64 wt.%.) reflect the absence of cryptomelane in the studied samples and possibly also the leaching of K to form illite, which is widespread as hydrothermal alteration at MdM (Madondo et al., 2020). Na₂O (<0.2 wt.%) concentrations are very low, reflecting the presence of minor amounts of Na bearing minerals like birnessite and/or smectites (Table 1; Madondo et al., 2020).

Low TiO₂ (<0.035 wt.%) concentrations indicate limited lithogenic components whereas the moderate Al₂O₃ (<1.9 wt.%) concentrations may be reflecting presence of hydrothermal kaolinite that is abundant at MdM (Madondo et al., 2020). The Al₂O₃ concentrations in the MdM jasperoids may also be representing the detrital aluminosilicate fraction from the replaced host rock, as reflected by the positive correlation between Al₂O₃ vs. TiO₂, MgO, CaO and K₂O (r: 0.66, 0.94, 0.81 and 0.72, respectively; Table 3) (Hein et al., 2000).
The Loss on Ignition (LOI) varies from 0.55 to 13.45 % (Table 2), representing mostly the water content of the jasperoids. However, this water is associated with the content of the Mn oxides in the jasperoids and not with chalcedony, as might be expected. Manganese oxides, particularly birnessite and todorokite, frequently contain water in their crystal lattice (e.g. Post, 1999). A near perfect positive correlation exists between MnO and LOI ($r = 0.98$; Table 3). On the contrary, a marked negative correlation occurs between SiO$_2$ and LOI ($r = -0.96$; Table 3). A possible cause for the negative correlation could be the fact that SiO$_2$ mainly exists as quartz rather than the often water-bearing chalcedony. Furthermore, MnO and SiO$_2$ show a high negative correlation ($r = -0.98$), which reflects their co-occurrence as the dominant constituents of the jasperoids. K$_2$O show negative correlations with SiO$_2$ and Fe$_2$O$_3$(tot) ($r: -0.40$ and $-0.70$, respectively). These correlations probably reflect the jasperoid replacement of K feldspar in the host rocks. Fe$_2$O$_3$(tot) shows a weak negative correlation CaO ($r = -0.48$) with, reflecting the replacement of carbonate during jasperoid formation. Mn and Fe$_2$O$_3$(tot) are negatively correlated ($r = -0.52$) reflecting the geochemical fractionation of Fe and Mn in the hydrothermal precipitates.

The weak positive correlation between SiO$_2$ and Fe$_2$O$_3$ contrasts with the strong negative correlation between SiO$_2$ and MnO. The weak correlation between SiO$_2$ and Fe$_2$O$_3$ is due to the co-precipitation of Si and Fe during jasperoid formation. This correlation can also due to the weak adsorption of SiO$_2$ on iron oxides (Anderson and Benjamin, 1985; Taylor, 1995; Pokrovski et al., 2003).

**Trace elements**

Trace element contents of MdM jasperoids are highly variable (Table 4). In comparison to the upper continental crust, samples exhibit a general enrichment in elements such as Ba (<96620 ppm), Sr (<1999 ppm), As (103 ppm), Cr (<640 ppm), Mo (>100 ppm), Sb (<10.4 ppm), Ge (<26 ppm), Ni (<110 ppm), Zn (<140 ppm), and Cu (<200 ppm), and are depleted in elements such as Pb (<12 ppm), Sn (<1 ppm), Ta (<0.1 ppm), Th (<0.6 ppm) and Rb (<29 ppm) (Figure 9). Co (15 ppm), W (<4 ppm) and V (<128 ppm) have average values close to those of the upper continental crust.

Most trace elements (Ba, Ni, Co, Zn, Cu, Ga, U, Mo and As) in the MdM jasperoids are particularly enriched in the manganiferous jasperoids. In fact, the most trace element-rich samples (MM-105A; MM-101; MMT-1) are those with the highest Mn content (Table 2). Sample MM-108, the most hematite-rich sample (Table 1), is depleted in trace elements compared with the Mn-rich samples, which suggests a control of the trace elements content by Mn oxides. Among the trace metals, only Cr shows preference for the hematitic jasperoids. The enrichment of Cr in the hematitic jasperoids is consistent with the one reported in Fe-rich hydrothermal precipitates.
Elevated Ba and Sr concentrations of the MdM jasperoids reflect the occurrence of barite in veinlets. Barium is also a dominant tunnel cation in manganese oxide minerals such as hollandite (Miura et al., 1987). High Ni and moderate Zn concentrations in samples MM 101 and MM 105A are consistent with enrichment of these elements in hydrothermal manganese rich deposits (Hein et al., 1997). Zinc concentrations are similar to those reported in other jasperoids of the Central Plateau (Labarthe-Hernandez et al., 1992). Low Pb and Cu concentrations indicate lack of sulfides in the deposit or significant sulfide precipitation at greater depths (e.g. Hein et al., 2000).

Co and Ni show a good correlation with Zn ($r = 0.91$ and 0.64, respectively; Table 5), as has been reported for other Mn-rich deposits (Hein et al., 2000). Similarly, Mo and V are correlated with Ba ($r = 0.92$ and 0.99, respectively; Table 5), which suggests that these metals probably occur in minerals that co-precipitated (e.g. McLemore et al., 1999). The lack of correlation between Cu and Pb with Zn ($r = 0.02$ and 0.33, respectively; Table 5) is further evidence of absence of sulfides (chalcopyrite, galena, sphalerite) or at least lack of co-precipitation (e.g. Hein et al., 2000).

**REE geochemistry**

Total REE (CREE) contents are low, ranging from 7.7 to 55.2 ppm, with an average of 26.9 ppm (Table 6). Samples are enriched in LREE compared with MREE ($\text{La}_{2}\text{O}_3/\text{Sm}_{2}\text{O}_3$ ratio = 2.47 to 6.47) and HREE ($\text{La}_{2}\text{O}_3/\text{Yb}_{2}\text{O}_3$ = 1.71 to 10.33). MREE are just slightly enriched over HREE ($\text{Gd}_{2}\text{O}_3/\text{Yb}_{2}\text{O}_3$ = 0.43 to 3.00); however, samples MM-108 and MM-13 show a marked enrichment in HREE. Ce anomalies are negative, ranging from 0.2 to 0.8, whereas Y anomalies ($Y_{\text{PASS}}/Y_{\text{PAAS}}$) range from 0.37 to 1.47. Eu anomalies are variable, ranging from 0.6 to 1.7.

**DISCUSSION**

Silica-rich precipitates such as jaspers, bedded cherts, hydrothermal cherts and syngenetic cherts are often difficult to differentiate macroscopically (Baltuck, 1982). Most silica-rich precipitates, however, frequently contain non-silica phases whose mineralogy and geochemical signature can be used to determine the origin of the precipitates and thus differentiate them (Jones and Murchey, 1986; Murray, 1994). The mineralogy, chemical composition and element associations of the MdM jasperoids are therefore investigated to shed new light on their conditions of formation and origin.

**Geochemical signatures**

The major- and trace-elements chemistry of the MdM jasperoids is characterized by high Si, Fe and Mn contents and low trace element concentrations. The latter reflects the low compatibility of quartz
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Figure 8. Photomicrographs showing the different quartz textures in the jasperoids of the Montaña de Manganeso deposit: (a) Cryptocrystalline quartz. (b) Microcrystalline quartz. (c) Coarse crystalline quartz. (d, e) Chalcedony transitioning to anhedral crystalline quartz, forming concentric colloform banding. (f, g) Quartz veins crosscut a jasperoid sample. The fractures are filled by a thin layer of first generation of microcrystalline quartz followed by coarse crystalline quartz. (h) Rare euhedral quartz grains. (i) Coarse crystalline quartz, consisting of crystals with planar and curved contacts. The dark dots are pores within the quartz crystals. Fe-Mn oxides particles replace different generations of quartz and fill spaces between quartz grain boundaries.

to incorporation of impurities (Heaney, 1994; Renault et al., 1995; McLemore et al., 1999). Unlike jasperoids from the southwest USA that are commonly associated with Carlin-type deposits (Nelson, 1990; Theodore and Jones, 1992; Arehart, 1996), the analyzed jasperoids from the MdM have high concentrations of manganese oxides and a depleted base metal content. Nonetheless, they have lower overall abundances of Sb, As, and Au than the Carlin type deposits (Theodore and Jones, 1992; Arehart, 1996; Stenger et al., 1998). Due to their enrichment in As, Sb, Zn, Mo, Ni, and Cr, the jasperoids from the MdM have a geochemical signature more similar to that of submarine hydrothermal manganese deposits (Hein et al., 1997, 2000).

A striking geochemical characteristic of the MdM jasperoids is the

Table 1. Results of powder X-ray diffraction (XRD) analysis showing major mineralogical compositions and their abundance (weight percent, semiquantitative).

| Mineral    | Manganese ore | Black jasperoids | Red jasperoids |
|------------|---------------|------------------|---------------|
|            | MM 105A      | MM 103           | MM 25C        | MM T2         | MM 106A      | MM 101      | MM 13       | MM 202      | MM 203      | MM 108      | MM 23       |
| Hematite   | 15            | 9                | 2             | 2             | 5            | 6           | 2           | 16          | 2           |             |             |
| Magnetite  | 11            | 3                | 21            | 71            | 78           | 78          | 5           | 12          |             |             |             |
| Goethite   |               |                  | 11            | 3             |              |             |             |             |             |             |             |
| Quartz     | 16            | 71               | 98            | 78            | 71           | 71          | 5           | 12          |             |             |             |
| Cristobalite | 25         |                  |               | 71            | 78           | 71          | 5           | 12          |             |             |             |
| Tridymite  |               |                  |               | 11            | 3            | 17          | 4           |             |             |             |             |
| Pyrite     |               |                  |               | 11            | 4            | 10          |             |             |             |             |             |
| Barite     | 39            |                  |               | 17            | 78           | 78          | 71          | 71          | 71          | 78          | 78          |
| Hollandite |               |                  |               | 11            | 3            | 17          | 4           |             |             |             |             |
| Pyrolusite |               |                  |               | 11            | 4            | 10          |             |             |             |             |             |
| Todorokite |               |                  |               | 2             | 78           | 78          | 71          | 71          | 71          | 78          | 78          |
| Birnessite | 11            |                  |               | 2             | 78           | 78          | 71          | 71          | 71          | 78          | 78          |
et al. potential sources of silica include biogenic, diagenetic, detrital and hydrometamorphic in origin (Roy, 1981, 1997). At MdM, field, petrographic and geochemical evidence indicate that hot hydrothermal solutions ascending from depths along faults and fractures supplied at least part of the silica and Fe-Mn for jasperoid formation.

Source of silica and Fe-Mn oxides

Determination of the sources or origin of SiO2, Fe and Mn is fundamental to understanding the genesis of the MdM jasperoids. Major potential sources of silica include biogenic, diageneric, detrital and hydrothermal (Sugisaki et al., 1982; Adachi et al., 1986; Yamamoto, 1986), whereas for manganese and iron oxides they can be hydrothermal, hydrogenetic and diageneric in origin (Roy, 1981, 1997). At MdM, field, petrographic and geochemical evidence indicate that hot hydrothermal solutions ascending from depths along faults and fractures supplied at least part of the silica and Fe-Mn for jasperoid formation.

Table 2. Summary of major element concentrations. For the chemical ratios calculations, atomic contents were recalculated from element concentrations (wt%).

|                  | SiO2 (%) | Al2O3 (%) | Fe2O3 (%) | MnO (%) | MgO (%) | CaO (%) | Na2O (%) | K2O (%) | TiO2 (%) | P2O5 (%) | LOI (%) | Total Fe/Mn | (Fe+Mn)/Ti | Al/(Al+Mn+Fe) | Si/Al |
|------------------|----------|-----------|-----------|---------|---------|---------|-----------|---------|----------|----------|---------|-------------|------------|----------------|-------|
| MM-106A          | 75.92    | 0.50      | 7.72      | 12.44   | 0.08    | 0.81    | <0.01     | 0.04    | 0.002    | 0.03     | 3.07    | 99.84       | 0.56       | 12539.26       | 0.02  |
| MM-101           | 41.12    | 1.69      | 2.77      | 59.69   | 0.33    | 0.56    | 0.11      | 0.40    | 0.025    | 0.18     | 13.45   | 83.33       | 0.04       | 3213.81        | 0.02  |
| MM-13            | 84.32    | 0.24      | 13.21     | 0.08    | 0.02    | 0.03    | <0.01     | 0.02    | 0.012    | 0.02     | 0.55    | 98.42       | 152.95     | 1292.79        | 0.01  |
| MM-202           | 71.86    | 0.24      | 15.64     | 7.26    | 0.07    | 0.24    | 0.03      | 0.05    | 0.001    | 0.10     | 2.08    | 97.57       | 1.95       | 27628.42       | 0.01  |
| MM-203           | 83.98    | 0.82      | 9.22      | 3.53    | 0.10    | 0.18    | 0.10      | 0.08    | 0.035    | 0.15     | 1.73    | 99.92       | 2.36       | 437.69         | 0.05  |
| MM-108           | 65.53    | 0.45      | 32.09     | 1.44    | 0.03    | 0.17    | <0.01     | 0.02    | 0.020    | 0.14     | 0.75    | 100.6       | 20.13      | 1965.06        | 0.01  |
| MM-23            | 91.96    | 1.90      | 1.57      | 0.51    | 1.46    | 0.05    | 0.64      | 0.02    | 0.027    | 0.01     | 2.21    | 100.50      | 8.39       | 75.93          | 0.45  |
| MM-105A          | 1.52     | 0.40      | 1.31      | 72.20   | 0.04    | 0.34    | 0.15      | 0.36    | 0.001    | 0.27     | 12.35   | 88.93       | 0.02       | 94803.55       | 0.00  |
| MMT-I            | 10.07    | 0.47      | 4.30      | 57.68   | 0.16    | 0.50    | 0.20      | 0.42    | 0.002    | 0.18     | 12.05   | 86.04       | 0.07       | 39766.88       | 0.01  |

Table 3. Correlation coefficient (r) matrix of various major elements of the Montaña de Manganeso jasperoids.

|        | SiO2 | Al2O3 | Fe2O3(tot) | MnO | MgO | CaO | K2O | TiO2 | P2O5 |
|--------|------|-------|-------------|-----|-----|-----|-----|------|------|
| SiO2   | 1.00 |       |             |     |     |     |     |      |      |
| Al2O3  | -0.02| 1.00  |             |     |     |     |     |      |      |
| Fe2O3(tot) | 0.38 | -0.46 | 1.00        |     |     |     |     |      |      |
| MnO    | -0.98| 0.06  | -0.55       | 1.00|     |     |     |      |      |
| MgO    | 0.00 | 0.94  | -0.52       | 0.05| 1.00|     |     |      |      |
| CaO    | 0.01 | -0.81 | -0.48       | 0.05| 0.93| 1.00|     |      |      |
| K2O    | -0.41| 0.72  | -0.70       | 0.49| 0.83| 0.89| 1.00|      |      |
| TiO2   | 0.33 | 0.66  | 0.05        | -0.35| 0.48| 0.34| 0.16| 1.00|      |
| P2O5   | -0.83| -0.14 | -0.14       | 0.79| -0.24| -0.18| 0.18| -0.12| 1.00|
The element ratios discussed so far are commonly coupled with discrimination diagrams to differentiate between hydrothermal, hydrogenous and diagenetic silica rich deposits (Adachi et al., 1986; Yamamoto, 1986; Yongzhang et al., 1994). For the Fe-Mn rich type additional discrimination diagrams have also been proposed (Bonatti et al., 1972; Toth, 1980; Choi and Hariya, 1992; Nicholson, 1992; Conly et al., 2011; Bau et al., 2014). These diagrams are adapted here to determine the sources of silica and Fe-Mn oxides for the MdM jasperoids (Figure 10). Uranium and Th concentrations of the MdM jasperoids are comparable to those of cherts of hydrothermal origin (Crerar et al., 1982; Hein et al., 1987; Flohr and Huebner, 1992), and effectively plot within or close to the hydrothermal field of Bonatti et al. (1976) on the U-Th binary diagram (Figure 10a). On the Fe-Mn-Al, Ni-Co-Zn and Fe-Mn-(Co+Ni+Cu) ternary diagrams all samples also fall within the hydrothermal field (Figure 10b-10d).

The chondrite-normalized REE patterns (REECN) (Figure 11) of the jasperoid samples partly reflect transition of some manganiferous jasperoids to Mn ore. The low Al/(Al+Fe+Mn) ratio for the MdM jasperoids (0.01–0.05 with one anomalous value of 0.45) likewise suggests predominant hydrothermal source. The Al/(Al+Fe+Mn) ratio of siliceous rocks ranges from as low as 0.01 for pure hydrothermal precipitates to as high as 0.60 for pure pelagic biological precipitates (Adachi et al., 1986; Yamamoto, 1986).

Table 4. Trace element composition of the jasperoids from the Montaña de Manganeso deposit.

| Sample | Sc  | V   | Ba  | Sr  | Y   | Zr  | Cr  | Co  | Ni  | Cu  | Zn  | Ti  | Ge  | As  | Rb  | Nb  | Mo  | Ag  | Sn  | Sb  | Cs  | Hf  | W   | Pb  | Th  | U   |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| MM-106A | <1  | 22  | 4017 | 70  | 4   | 3   | 280 | 3   | 20  | 200 | 30  | <0.1| 6   | 5   | 29  | <1  | 13  | <0.5| <1  | 0.8 | <0.5| <0.2| <1  | <5  | <0.1| 0.6 |
| MM-101  | 2   | 126 | 96620| 1768| 15  | 12  | <20 | 15  | 110 | 60  | 140 | 0.1 | 26  | 81  | 2   | 1   | 95  | <0.5| <1  | 9   | <0.5| 0.3 | 2   | <5  | 0.3 | 6.2 |
| MM-13   | <1  | 40  | 17310| 180 | <1  | 5   | 640 | 1   | <20 | <10 | <30 | <0.1| 6   | 8   | 2   | <1  | 24  | <0.5| <1  | 2.4 | <0.5| <0.2| 1   | <5  | 0.2 | 0.2 |
| MM-202  | <1  | 58  | 7266 | 145 | 3   | <2  | 330 | 3   | 50  | 40  | 90  | <0.1| 6   | 74  | <2  | <1  | 13  | <0.5| <1  | 4   | <0.5| <0.2| 3   | 5   | <0.1| 1   |
| MM-203  | 1   | 54  | 3741 | 105 | 9   | 12  | 330 | 3   | 30  | 20  | 40  | <0.1| 5   | 28  | 2   | <1  | 6   | <0.5| <1  | 1.7 | 0.9 | 0.2 | <1  | <5  | 0.3 | 0.4 |
| MM-108  | <1  | 128 | 2079 | 59  | 4   | 7   | 340 | 2   | <20 | <10 | <30 | <0.1| 6   | 20  | <2  | <1  | 27  | <0.5| <1  | 5   | <0.5| <0.2| 4   | 5   | 0.1 | 0.4 |
| MM-23   | 1   | 12  | 554  | 63  | 4   | 16  | 480 | 2   | <20 | <10 | <30 | <0.1| 1   | 5   | <1  | <29 | 1   | 4   | <0.5| <0.1| <0.5| <0.1| 1.1 | 0.3 | 1   | 11  | 0.6 | 0.2 |
| MM-105A | 2   | 102 | 43710| 1999| 14  | 4   | <20 | 11  | 70  | 50  | 140 | 0.1 | 7   | 103 | <2  | <1  | 100 | <0.5| <1  | 10.4| <0.5| <0.2| 2   | 12  | <0.1| 3.9 |
| MMT-I   | <1  | 102 | 24480| 1519| 19  | 3   | <20 | 8   | 80  | 80  | 120 | <0.1| 7   | 78  | 2   | <1  | 39  | <0.5| 1   | 2.1 | <0.5| <0.2| <1  | 5   | <0.1| 5.2 |

Figure 9. The Upper Continental Crust (Taylor and McLennan, 1985) normalized elemental distribution pattern of the Montaña de Manganeso jasperoids.
Y anomalies (YPASS/HoPASS >1) are typical of hydrothermal Fe-Mn deposits whereas hydrogenetic Mn deposits form negative anomalies (YPASS/HoPASS <1) (Bau et al., 2014). Rare Earth elements plus Yttrium (REY) compositions of the Montaña de Manganeso jasperoids. Eu, Ce and Y anomalies are also shown in Table 6.

|   | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | Y | YPASS/HoPASS | ΣREE | Eu/Eu* | Ce/Ce* |
|---|---|----|---|----|----|----|----|----|----|----|----|----|----|----|----|-------------------|-------|--------|-------|
| MM-106A | 1.5 | 1.7 | 0.37 | 1.7 | 0.4 | 0.16 | 0.6 | 0.1 | 0.5 | 0.1 | 0.3 | 0.22 | 1.5 | 0.22 | 1.5 | 1.38 | 55.2 | 1.7 | 0.5 |
| MM-101 | 10.5 | 8.9 | 1.72 | 7.9 | 1.7 | 1.11 | 2.4 | 0.3 | 1.9 | 0.4 | 1.4 | 0.22 | 1.5 | 0.22 | 15 | 1.38 | 55.2 | 1.7 | 0.5 |
| MM-13 | 1.2 | 1.5 | 0.25 | 1.0 | 0.3 | 0.21 | 0.5 | 0.1 | 0.4 | 0.1 | 0.4 | 0.08 | 0.7 | 0.72 | 1 | 0.37 | 7.7 | 2.1 | 0.7 |
| MM-202 | 3.1 | 1.7 | 0.65 | 2.5 | 0.5 | 0.21 | 0.5 | 0.1 | 0.5 | 0.1 | 0.3 | 0.05 | 0.3 | 0.05 | 0.3 | 1.10 | 13.6 | 1.3 | 0.3 |
| MM-203 | 5.9 | 5.6 | 1.45 | 6.3 | 1.4 | 0.38 | 1.5 | 0.2 | 1.4 | 0.3 | 0.8 | 0.13 | 0.8 | 0.14 | 10 | 1.10 | 35.3 | 0.8 | 0.5 |
| MM-108 | 1.7 | 2.8 | 0.47 | 1.9 | 0.4 | 0.09 | 0.5 | 0.1 | 0.7 | 0.2 | 0.5 | 0.1 | 0.8 | 0.13 | 0.4 | 0.73 | 14.4 | 0.6 | 0.8 |
| MM-23 | 2.3 | 3.4 | 0.61 | 2.4 | 0.5 | 0.09 | 0.5 | 0.1 | 0.6 | 0.1 | 0.4 | 0.06 | 0.4 | 0.6 | 0.4 | 1.47 | 15.5 | 0.6 | 0.7 |
| MM-105A | 3.7 | 2.3 | 1.09 | 5.3 | 1.5 | 0.7 | 2.1 | 0.3 | 2.3 | 0.5 | 1.5 | 0.25 | 1.6 | 0.28 | 14 | 1.03 | 37.4 | 1.2 | 0.3 |
| MMT-I | 9.7 | 3.2 | 1.49 | 6.9 | 1.5 | 0.62 | 2.1 | 0.3 | 2.2 | 0.5 | 1.6 | 0.24 | 1.5 | 0.25 | 19 | 1.39 | 51.1 | 1.1 | 0.2 |

It is known that the replacement of limestone by silica, generally necessary for jasperoid formation (Lovering, 1972; Theodore and Jones, 1997), suggests that the oxidized iron minerals (hematite, goethite and magnetite) resulted from oxidation of pyrite (Schwertmann and Murad, 1983; Chi Fru et al., 2018). The existence of only manganese oxides with no Mn<sup>2+</sup> bearing minerals indicates formation at a later stage, under oxidizing conditions.

A cooling intrusive at depth possibly served as the driving force for deep circulating hydrothermal fluids that deposited silica in Fe-Mn oxides. Labarthe-Hernández et al. (1992) considered the felsic El Socorro intrusive, exposed about 55 km to the SW of the MdM, as the cause of the formation of the main known jasperoids of the region. The Cenozoic volcanism linked in certain parts of the Central Plateau to the volcanism of the Sierra Madre Occidental (Aranda-Gómez and Mcdowell, 1998; Aranda-Gómez et al., 2007; Tristán-González et al., 2008, 2009a; Aguillón-Robles et al., 2009; Rodriguez-Ríos et al., 2013) could have supplied the vast amounts of silica required for the formation of the jasperoid of the Central Plateau, including those of the MdM.

Table 6. Rare Earth elements plus Yttrium (REY) compositions of the Montaña de Manganeso jasperoids. Eu, Ce and Y anomalies are also shown in Table 6.
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CONCLUSIONS

The MdM jasperoids occur as primarily fault-controlled blocky and lenticular bodies of diverse sizes confined to NE-trending faults within strongly folded and fractured sedimentary and volcaniclastic rocks. There is field, petrographic and geochemical evidence that hot hydrothermal solutions ascending from depths along faults and fractures supplied silica and at least part of the manganese and iron oxides for jasperoid formation. The presence of a feeder fault system, well-manifested differentiation of Mn from Fe and Si, banded and brecciated jasperoids, with associated zones of argillic alteration strongly suggest formation by hydrothermal processes close to the paleosurface. Textural evidence indicates multiple episodes of replacement, brecciation, and veining by episodic injection of silica-rich hydrothermal fluids. The geochemical signature of the jasperoids also suggest that silicification was product of hydrothermal activity. Silica and Fe-Mn oxyhydroxides were likely precipitated from cooling ascending silica-rich hydrothermal fluids that evolved from reduced to oxidized. The hydrothermal fluids filled faults and fractures, and penetrated permeable horizons and replaced favorable units forming massive jasperoid bodies. The ascending hot hydrothermal solutions leached trace metals from the host rocks, part of which were scavenged by Fe and Mn oxides. An intrusive at depth probably served as a driving force for deep circulating hydrothermal fluids that deposited silica and Fe-Mn oxides.

Figure 10. Discriminating diagrams for the Montaña de Manganeso jasperoid samples. (a) U-Th discrimination diagram. The Montaña de Manganeso jasperoids fall within and close to the hydrothermal field. Fields after Bonatti et al., (1976). (b) Al-Fe-Mn ternary diagram showing the fields of hydrothermal and hydrogenous precipitates. The Montaña de Manganeso samples all fall within the hydrothermal field. Fields after Adachi et al. (1986) and Yamamoto (1987). (c) Zn-Ni-Co ternary diagram showing fields of hydrothermal and hydrogenous deposits. Fields after Choi and Hariya (1992). The Montaña de Manganeso samples all fall within the hydrothermal field. (d) On the (Co+Ni+Cu)-Fe-Mn ternary diagram (fields after Bonatti et al., 1972; Toth, 1980) the Montaña de Manganeso samples also fall within the hydrothermal field.

Figure 11. Chondrite normalized REE patterns displaying fields of hydrothermal and hydrogenetic deposits. The Montaña de Manganeso samples mostly fall below the hydrothermal field.
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