New age in the geological evolution of the Cerro de Mercado Iron Oxide Apatite deposit, Mexico: Implication in the Durango apatite standard (DAP) age variability

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ABSTRACT

Cerro de Mercado Iron Oxide Apatite deposit (CM-IOA) is known as a classical example of an IOA deposit worldwide and is also probably the most prolific locality in terms of gem-quality fluorapatite. The CM-IOA deposit is located in the Chupaderos Caldera Complex (CCC), a large rhyolitic volcanic center belonging to the Upper Volcanic Supergroup of Oligocene age. The main Cerro de Mercado IOA mineralization body is crosscut by a kilometer long rhyodacite dyke that acted as channelway for the rhyodacite flow. The rhyodacite dyke crosscuts all the volcanic sequence. K-Ar ages of this dyke range from ca. 28 to 27 Ma. Apatite in the Cerro de Mercado deposit appears in two different positions, (1) altered crystals intergrown with martite within massive mineralization, with or without diopside; and (2) on martite in degassing cavities and fracture zones, with accompanying chaledony and calcite. Crystallization of the apatite phase was complete prior to the eruption of the overlying felsic flows of the Tinaja Member of the Cacaria Formation at ca. 31.44 Ma and preserve of potential late thermal event (McDowell et al., 2005). The mean ages reported by numerous and different isotopic methods for the fluorapatite DAP are coincident within the margins of uncertainty with the volcanic host rocks ages. But DAP ages reported present a significant variability of up to 8%. Such variability is also found in all dating technics applied in Durango Apatite (fission-track, U/Pb and (U-Th)/He ages) and suggest a thermal resetting related to the late volcanic event at 28-27 Ma.

1. Introduction

Cerro de Mercado Iron Oxide Apatite deposit (CM-IOA) is located in the City of Durango (Durango State, Mexico), at the boundary between the Sierra Madre Occidental volcanic province (SMO) at West, and Mesa Central at East. Cerro de Mercado deposit is known worldwide as a classical example of an IOA deposit and is also probably the most prolific locality in terms of gem-quality fluorapatite (Foshag, 1928; Young et al., 1969; Lyons, 1988; Corona-Esquivel and Henriquez, 2004; Henriquez and Corona-Esquivel, 2000). The Durango apatite or DAP is relatively free of fluid and solid inclusions, and their crystals can easily attain a centimeter in diameter. These famous yellow-green fluorapatite crystals are instantly recognizable and commonly used as mineralogical (Mauthner and Ottaway, 2015), geochemical (Boyce and Hodges, 2005; Marks et al., 2012; Kusebauch et al., 2015; Holger et al., 2015; Mao et al., 2016; Sun et al., 2016; Chew et al., 2016; Müller and Anckzewicz, 2016; Tacail et al., 2016; Gerin et al., 2017) and fission-track and (U-Th-Sm)/He thermochronometry (Zeitler et al., 1987, 2017; House et al., 1999; Ravenhurst et al., 2003; McDowell et al., 2005; Abdullin et al., 2014; Willett et al., 2017; Recanati et al., 2017; Li et al., 2018; Jonckheere et al., 2018; McDannell et al., 2018) standards. Zeitler et al. (1987) selected these apatites to set the base for thermochronometric studies. Even though the results showed straightforward and reproduciblediffusive behavior of ^4He in the Durango fluorapatite (Zeitler et al., 1987), the conventional furnace and laser fusion (U-Th)/He dating of small DAP fragments yield apparent ages that vary by more than 8% (House et al., 1999). The fission-track (TF) variability ages could be reduced from 22 to 31 Ma to 32-28 Ma after analytical correction but do not disappear (Jonckheere et al., 2015). Several authors regularly comment the heterogeneous geochronological and isotopic behavior of the Durango apatite standard (i.e. House et al., 1999; Chew and Donelick, 2012; Abdullin et al., 2014).
The entire Chupaderos Caldera complex was formed in a surprisingly brief period of volcanic activity (less than 1 m.y., McDowell et al., 2005), pinning down the IOA mineralization and related apatite precisely within the analytical errors of the applied absolute dating method (McDowell et al., 2005).

The DAP is considered as an international geochronological and mineralogical standard. Some relatively old geological reports on these apatites are available (Foshag, 1928; Young et al., 1969; Lyons, 1988; Henríquez and Corona-Esquivel, 2000; Corona-Esquivel and Henríquez, 2004) but none of them present detailed geological and mineralogical descriptions of the Cerro de Mecardo IOA deposit.

The aim of this paper is to summarize the geologic settings of the Cerro de Mercado IOA deposit, providing some new geological and paragenetical evidences and a new volcanic K-Ar age in order to bring novel geological contributions in the apatite geochronological heterogeneity discussion.

2. Geological setting

The Cerro de Mercado iron deposit is located in the central-eastern part of the Sierra Madre Occidental province (SMO; McDowell et al., 1997, 2005; Ferrari et al., 2007, 2013; Savage and Wang, 2012). The SMO constitutes the largest silicic igneous province in North America and the most recent event of this kind on Earth (Ferrari et al., 2007). The volcanic column is traditionally divided into two members known as Upper and Lower Volcanic Supergroups (McDowell et al., 2005, 2012; Ferrari et al., 2007, 2013; Savage and Wang, 2012). The Upper Volcanic Supergroup (UVS), that overlies the Lower Volcanic Complex (LVC) formed by a series of Late Cretaceous to early Eocene batholithic rocks and intermediate lavas (McDowell et al., 2005, 2012; Ferrari et al., 2007, 2013; Savage and Wang, 2012), is composed by a thick, late Eocene to early Miocene ignimbrite that covers most of the province. The UVS was emplaced between ca. 38-18 Ma, it is bimodal and made up mostly by rhyolitic ignimbrites, local rhyolitic domes and basaltic lavas intercalations. Detailed geochronological studies recognized two main flare-up events at ca. 34 - 28 Ma and ca. 24 - 18 Ma respectively (Ferrari et al., 2007, 2013). The Oligocene episode (ca. 34 - 28 Ma; including the Cerro de Mercado volcanic sequence and IOA member) forms up to 75% of the volcanic erupted volume. The Miocene ignimbritic pulse (ca. 24 - 18 Ma) is limited to the southwestern and western parts of the SMO and Baja California, (Ferrari et al., 2007, 2013). SMO in western Durango is composed by a plateau of flat lying ignimbrites, which appears to be unfaulted (Ferrari et al., 2007, 2013). On both flanks of this undeformed core, extensional fault systems tilted the ignimbrite succession in different directions, passing from crustal thickness of around 55 km in the ignimbrites core to 35 km in the...
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is a heterogeneous mixture of volcanic
followed by a collapse of the broader caldera area and the concomitant
by an autolithic breccia known as the Aguila unit. This eruption was
eruption originated an 8-km diameter central vent zone characterized
into three members, (1) the Leona Member that comprises felsic
volcanoclastic tu
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into three members, (1) the Leona Member that comprises felsic flow
domes, local ash flows and air-fall tuffs; (2) The Mercado Iron Member, that includes the iron oxide and apatite (IOA) ore deposits, associated to felsic plugs and breccias, emplaced over an erosional unconformity; and (3) The Tinaja Member formed by felsic flows that cover the main IOA ore body (Fig. 1; Lyons, 1988). A second major eruption at the CCC deposited the Santuario ignimbrite, a light gray crystal-vitrified welded tuff over the Cacaria Formation. The eruption of the Santuario ignimbrite apparently occurred through a system of vents distributed throughout the caldera area, causing a small collapse. After this ignimbrite eruption, the activity of the caldera was more discreet. The Santa Maria Formation, a thin densely welded vitric ignimbrite, erupted from a 16-km-diameter collapse zone in the center of the caldera. It was followed by the eruption of the Caleras basalts located at the southern caldera margin (McDowell et al., 2005). 40Ar/39Ar absolute dating of Santuario and Aguila (sanidine, feldspar; McDowell et al., 2005) indicates a short time interval of volcanic activity, from 31.59 ± 0.11 to 31.44 ± 0.20 Ma (McDowell et al., 2005). The main IOA mineralization body was crosscut by a kilometric long rhyodacite dyke that fraction between 250 and 400
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μ

3. Experimental methods

Two dyke samples, the first located at the southwestern end and the second at the central part of the deposit (Fig. 1), were dated by the K-Ar method at the Noble Gas Laboratory of the Institute of Geology, Universidad Nacional Autónoma de México (Table 2). These samples were fragmented to a size of less than 2 mm with a steel disk breaker. Subsequently, they were sieved into two fractions, 500-400 μm and 400-250 μm to choose the most suitable for clean matrix separation. The fraction between 250 and 400 μm was used. The matrix separation was carried out with a Frantz magnetic separator, and finally by hand picking.

The measurements of K were made following the procedure using an X-ray fluorescence spectrometer, model Siemens 3000 XRF, calibrated with international reference materials (Solé and Enrique, 2001). The results have an uncertainty of 1%. The argon was measured by isotopic dilution with a mass spectrometer MM1200B operated under static vacuum (Solé, 2009). The samples were fused with an infrared (CO2) laser in an ultra-high vacuum chamber. The gases were purified with a liquid nitrogen trap and two SAES solid state getters, one at room temperature and the other at 400 C. The signal was acquired with an electron multiplier. The relative standard deviations of the 40Ar, 38Ar and 36Ar isotopes are respectively < 0.1%, < 0.1% and < 0.5%. The data is reported with one standard deviation. The constants of Steiger and Jäger (1977) were used for the calculations.

Mineral phases and compositions were determined using a JEOL model 8900 Superprobe at the Binghamton University, NewYork, USA (Table 2).

4. New geochronological data of the Cerro de Mercado IOA deposit

The rhyodacite dyke did not receive sufficient attention by former authors while unraveling the age crosscutting relationships and suc-
cession in Cerro de Mercado iron deposit. For some authors, this dyke represents the feeding structure of the Oligocene Cacaria formation (Lazarre and Enrique, 2001). Later, it was interpreted as representing the last magmatic event that occurred in the Caldera (Corona-Esquivel and Henríquez, 2004). This dyke crosscuts all the

extended Eastern flank, close to CM-IOA deposit (McDowell et al., 2005, 2012; Ferrari et al., 2007, 2013).

The CM-IOA deposit sits in the Chupaderos Caldera Complex (CCC), a large rhyolitic volcanic center belonging to the UVS of Oligocene age (31.58 ± 0.16 to 31.44 ± 0.20 Ma, (Sanidine, 40Ar/39Ar; McDowell et al., 2005). The caldera volcanic products rest unconformably on top of the folded Cretaceous limestone units, with locally some intercalations of discontinuous conglomerates (Ahuichila Conglomerate) and Eocene andesite flows (McDowell et al., 2005). The Chupaderos Caldera eruption originated an 8-km diameter central vent zone characterized by an autolithic breccia known as the Aguila unit. This eruption was followed by a collapse of the broader caldera area and the concomitant deposition of the overlying Cacaria Formation (Lyons, 1988). The latter is a heterogeneous mixture of volcanic flows, ash flow, lava dome, and volcanoclastic tuffs. Apatite appears in two different positions, (1) altered crystal intergrown with martite within the massive mineralization, with or without diopside (Fig. 3A and B and Table 1); and (2) on top of martite in fumarolic degassing cavities and fracture zones, with chalcedony and calcite (Fig. 3C). The apatite crystallization overgrowths occur on the top and lateral limits of the magnetite ore body, probably from halogen-rich vapors (Dong, 2005). Crystallization of apatite was completed before eruption of the overlying felsic flows of the Santuario Formation (Figs. 1 and 2A-B; Corona-Esquivel and Henríquez, 2004). At present time, the mine workings allow to see that the emplacement of the deposit is structurally controlled by the intersection of two major faults of N-S and NE-SW trends that also host part of the breccia ore bodies (Figs. 1 and 2C).

Unaltered pyroxene related to primary apatite event have a homogeneous chemical composition (Table 1), crystallization temperatures ranging from 500 to 700 C (Lindsley, 1983). The Cerro de Mercado IOA pyroxene present a very low OH content (< 0.001%) suggesting rather a magmatic than hydrothermal origin. Apatite chemical composition, in terms of F, Cl, SO4, and OH, allow to classify them as F-apatite, poor in Cl, indicating a magmatic source (Corona-Esquivel and Henríquez, 2004). Cerro de Mercado magnetite samples are rich in V (up to 2400 ppm), and Mg (up to 2200 ppm) and poor in Ti (< 5000 ppm). Apatite, pyroxene and magnetite from Cerro de Mercado present similar composition than apatite, pyroxene and magnetite from the Cretaceous iron ores belt in Chile (Naslund et al., 2002) and Kiruna in Sweden (Nyström and Henríquez, 1994).

The IOA ore bodies are the result of subaerial volcanic processes that included the formation and eruption of volatile-rich iron oxide magmas, large scale fumarolic degassing and venting, and deposition of a conformable ash-like hematitic blanket in the surrounding area (Lyons, 1988; Naslund et al., 2002; Corona-Esquivel and Henríquez, 2004). Within the Chupaderos caldera all the other iron oxide ore deposits occur within the same general stratigraphic interval, and have been correlated as part of the "Mercado Iron Member" belonging to the Cacaria Formation (Lyons, 1988). Two different genetic processes have been proposed for this deposit. Some authors suggested an iron oxide-rich igneous melt that separated from a parental "oxide magma" in close relationship with the extrusion of silicic magmas, in a similar way as in El Laco deposit (Lyons, 1988; Naslund et al., 2002; Corona-Esquivel and Henríquez, 2004). Other, suggested the metasomatic replacement of previous volcanic rocks by massive oxide bodies triggered by hydrothermal fluids that vented-out onto the surface (Labarte et al., 1987; Megaw and Barton, 1999; Barton et al., 2000).

The different ore bodies present a fairly simple mineralogy, made up by magnetite and hematite with minor apatite, and silica. Fe-oxide bodies are surrounded by an aureole of argillic alteration (Lyons, 1988; Corona-Esquivel and Henríquez, 2004). Hydrothermal alteration locally transforms magnetite and hematite to martite (Corona-Esquivel and Henríquez, 2004). The intimate association of the apatite and iron ore, and the occurrence of both during local magmatism is unmistakable.
Oligocene units, including the entire iron deposit, with a general NE-SW direction and for a length of 1350 m, being almost vertical throughout the entire strike, with a variable thickness between 6 and 9 m (Figs. 1 and 2; Corona-Esquivel and Henríquez, 2004). In the central part, it was not possible to verify its continuity as the outcrop is covered by mine dumps.

This dyke is light pink colored. Macroscopic observation allow to discern a porphyritic texture. The matrix is constituted by submillimeter crystals of plagioclase, K-feldspar and quartz. The plagioclase and K-feldspar phenocrysts are mainly euhedral to subhedral with sizes between 0.5 and 2 mm. Minute quartz crystals, biotite and diopside are also observed. Some xenoliths of magnetite-hematite are incorporated, when the rhyolitic dyke crosscut the Fe-oxides bodies.

The matrix fractions used for K-Ar dating consists of an inseparable mixture of potassium feldspar, plagioclase and quartz. The plagioclase and K-feldspar phenocrysts are mainly euhedral to subhedral with sizes between 0.5 and 2 mm. Minute quartz crystals, biotite and diopside are also observed. Some xenoliths of magnetite-hematite are incorporated, when the rhyolitic dyke crosscut the Fe-oxides bodies.

The K-Ar results are presented in Fig. 4 and Table 2. The apparent ages for the rhyolitic dyke range from 27.3 to 28.1 Ma with analytical errors of ± 0.8 – 1.0 Ma.

5. Discussion

The origin of the Cerro de Mercado IOA deposit is intimately related to the Paleogene magmatism of the SMO, particularly with the development of the Caldera de Chupaderos (Lyons, 1988; McDowell et al., 2005; Corona and Henriquez, 2004). The age of the Cerro de Mercado volcanic sequence was established between 31.59 ± 0.11 and 31.44 ± 0.22 Ma (sanidine, 40Ar/39Ar; McDowell et al., 2005) and the age of the late apatite related to the Fe mineralization based on its relationship with the Oligocene enclosing rock and fission-track (31.2 ± 0.2 Ma; apatite monocrystal, FT-LAICPMS, Abdullin et al., 2014, Fig. 4) and (U–Th–Sm)/He ages (31.03 ± 0.44 Ma (apatite monocrystal, McDowell et al., 2005, Fig. 4). In this geological history, the Caracarias formation overlies the IOA mineralization at
The DAP population is preserved from late thermal/geochemical modifications. The time between bothapatite formation events and auto alteration of the previously deposited volcanic products. This late degassing event by

Table 1

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Table 2

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31.44 ± 0.22 Ma, fix a minimum age of the DAP, and suggest that the DAP population is preserved from late thermal/geochemical modifications. However, field relationship observations coupled with this new dyke K-Ar dating indicate that the CM-IOA Olivine deposit is crosscut by a younger Olivine volcanic event located at ca. 28-27 Ma. This fissural volcanism event is slightly younger, at local scale, in respect to the 30–31 Ma silicic explosive volcanism represented by the Chupaderos caldera. At a regional scale, it corresponds to the last large volcanic flare up of the SMO formation and marks the decrease in eruptive activity and heat anomaly observed between 28 and 25 Ma (Ferrari et al., 2007).

A detailed CM-IOA paragenetic sequence shows the occurrence of two differentapatite formation events. The firstapatite generation is coeval with the emplacement of the massive iron bodies, while the late second generation formed within fumarolic degassing fractures and voids with silica and carbonates. This late event probably marks the end of the iron rich magmatic event by final degassing of volatiles and auto alteration of the previously deposited volcanic products. This last generation is the most sought after for DAM due to their purity and very well crystalized shape. Bothapatite generations occur between the Aguila and Santuario Olivine volcanic formations, ca. 0.2 Ma (McDowell et al., 2005). The time between bothapatite formation is too short to be analytically defined.

Fig. 4 is a compilation of the different ages reported for the CM-IOA volcanic host rocks (Fig. 4A; McDowell et al., 2005, and this study) and absoluteapatite ages determined applying several analytical techniques (Fig. 4B-F). The 40Ar/39Ar ages for the volcanic host-rock formations of the Iron member define a thigh age range, comprised within the analytical error margin for the IOA (31.34 ± 0.01 and 31.51 ± 0.10 Ma; sandine 40Ar/39Ar age, McDowell et al. (2005); Fig. 4A). This volcanic succession is crosscut by the late dyke at ca. 28-27 Ma (this study) which marks the end of the Olivine volcanic activity in the region (Fig. 4A). Fig. 4B to G displays the published ages for the Durango fluorapatite using different analytical techniques. In general, the ages reported by different isotopic methods for volcanic rocks and DAP apatite are coincident within the margins of uncertainty and it can be summarized that to date the standard age for DAP apatite is still taken as 31.03 ± 0.44 (1σ) Ma (McDowell et al., 2005) or 31.4 Ma (Soile and Pi, 2005). But it is noteworthy that theapatite age range is quite wide, whatever the dating technique applied, from 33 to 27 Ma (Fig. 4). The PT-LAICPMS ages distribution range and errors are tighter than the conventional FT dating technique and are more comparable to the host rocks 40Ar/39Ar ages (from Fig. 4B and D). In brief, all dating techniques, including (U-Th)/He inter-laboratory age data (Fig. 4B-G), show a complex distribution that could be divided into two different populations, (1) a first population forming a well-defined family up to ca. 32 Ma, better defined in the U/Pb and conventional fission tracks methods and (2) a second population showing decreasing ages from ca. 31 to ca. 27 Ma (Fig. 4E). The same general decreasing evolution is observable in the distribution of the punctual PT-LAICPMS ages calculated for different DAP crystals and within a unique DAP crystal (Fig. 4G; modified from Abdullin et al., 2014; Jonckheere et al., 2015). Considering a fixedapatite composition (Boyece and Hodges, 2005; Chew et al., 2016; Mao et al., 2016; Sun et al., 2016), the most important impact factor for age modification should be the closing isotopic system temperatures, above 500 °C for the U/Pb system and above 150 °C for the (U-Th)/He system (Chew and Donelick, 2012). This discrete thermal event after apatite formation could induce some partial resetting in low temperature geochronometers like (U-Th)/He orapatite fission track. In the Cerro de Mercado IOA deposit, such late thermal event is represented by the late-Oligocene fissural volcanism event at ca. 28-27 Ma, which precisely displays the same age than the younger - resetted? apatite ages.
potential bias in analytical techniques. The probable thermal event is explained by a late thermal event at 28-27 Ma without considering apatite, suggesting that the age variation range observed in DAP could be related to the Chupaderos caldera, which strongly constrains the primary apatite crystallization age at 31.02 ± 0.22 Ma (McDowell et al., 2005) and K-Ar age of the rhyodacite dyke (this study); (B) Red and blue circles: (U/Th)He DAP ages (McDowell et al., 2005; Farley, 2002; House et al., 2000; Solé and Pi, 2005); (C) open circles: (U/Th)He DAP mean age by laboratory, Waikato, CSIRO, Curtin, Tübingen, Arizona, Yale, Caltech; (D) Red and blue triangles: DAP U/Pb dating (Chew et al., 2011, 2014; Chew and Donelick, 2012; Li et al., 2012; Thomson et al., 2012; Cochrane et al., 2014); (E) Red and blue diamonds: Fission Track LA-ICPMS dating compilation (Hasebe et al., 2004; Hadler et al., 2009; Soares et al., 2014; Abdullin et al., 2014); (F) Red and blue squares: Fission Track conventional dating compilation (Hurford and Gleadow, 1977; Green, 1978; Märk et al., 1980; Jonckheere et al., 1993, 2015; lunes et al., 2002); (G) Red and blue diamonds: Fission Track LA-ICPMS dating point in 12 different DAP crystals, (Abdullin et al., 2014). The green dotted area corresponds to the accepted DAP age variation (Abdullin et al., 2014 and references therein). Blue dots potentially unmodified ages; Red dots potentially resetted ages. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 4. Age comparison plot for Durango fluorapatite showing the single age variability and volcanic host-rocks bracketing ages; modified from Abdullin et al. (2014). (A) 40Ar/39Ar volcanic rocks, Sanctuario Fm. (green) and Carcara Fm (orange; McDowell et al., 2005), and K-Ar age of the rhyodacite dyke (this study); (B) Red and blue circles: (U/Th)He DAP ages (McDowell et al., 2005; Farley, 2002; House et al., 2000; Solé and Pi, 2005); (C) open circles: (U/Th)He DAP mean age by laboratory, Waikato, CSIRO, Curtin, Tübingen, Arizona, Yale, Caltech; (D) Red and blue triangles: DAP U/Pb dating (Chew et al., 2011, 2014; Chew and Donelick, 2012; Li et al., 2012; Thomson et al., 2012; Cochrane et al., 2014); (E) Red and blue diamonds: Fission Track LA-ICPMS dating compilation (Hasebe et al., 2004; Hadler et al., 2009; Soares et al., 2014; Abdullin et al., 2014); (F) Red and blue squares: Fission Track conventional dating compilation (Hurford and Gleadow, 1977; Green, 1978; Märk et al., 1980; Jonckheere et al., 1993, 2015; lunes et al., 2002); (G) Red and blue diamonds: Fission Track LA-ICPMS dating point in 12 different DAP crystals, (Abdullin et al., 2014). The green dotted area corresponds to the accepted DAP age variation (Abdullin et al., 2014 and references therein). Blue dots potentially unmodified ages; Red dots potentially resetted ages. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

determined in the IOA-CM deposit. The relative temporal proximity of the late magmatic event described in this work to the primary age of the fluorapatite combined with the analytical errors makes somewhat difficult to identify with certainty the resetting, if present, as we observe in Fig. 4B-G. This late Oligocene volcanism is fissural and the thermal affection induced to the DAP must be very heterogeneous at the deposit scale. As very few authors indicate the location of their apatites within the CM deposit it is so far impossible the estimate a size and intensity of the thermal affection aureole.

6. Conclusions

The volcanic history of the Cerro de Mercado IOA deposit is directly related to the Chupaderos caldera, which strongly constrains the primaryapatite crystallization age at 31.02 ± 0.22 Ma (McDowell et al., 2005). In this study we showed that the local volcanic history could be more complex and that a late volcanic event occurs in the Cerro de Mercado Fe district at ca. 27-28 Ma. Also we present field evidences of multistageapatite crystallization. The comparable age of the rhyolitic dyke and the (U-Th)/He and fission track younger ages determined in apatite suggest that the age variation range observed in DAP could be explained by a late thermal event at 28-27 Ma without considering potential bias in analytical techniques. The probable thermal affection of the DAP population is very heterogeneous at the deposit scale.

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