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Geochronological and geochemical constraints on the genesis of Cu-Au skarn deposits of the Santa María de la Paz district (Sierra del Fraile, Mexico)

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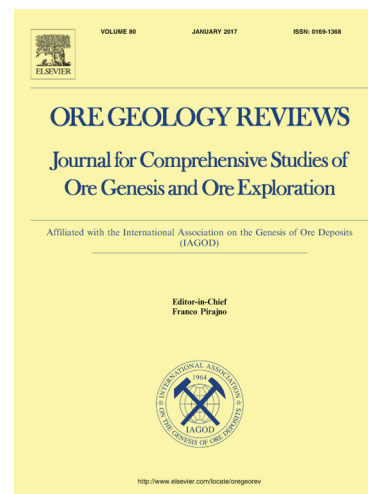Siegfried Siesgesmund[1], Rubén López-Doncel[2], Pascal Sieck[1,3], Hendrik Wilke[1], Klaus Wemmer[1], Dirk Frei[4,5], Sebastián Oriolo[6*]

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Abstract

Cu-Au skarn deposits of the mining district of Santa María de La Paz are located in the Sierra del Fraile, in the northern part of San Luis Potosí, Mexico. Samples of four different intrusions and their related skarn deposits were taken underground, in order to obtain whole-rock and mineral geochemical data. U-Pb LA-ICP-MS zircon data indicate crystallization ages of ca. 37.6-35.0 Ma for skarn-related granitic and granodioritic stocks, which show dominant metaluminous to slightly peraluminous, high-K calc-alkaline compositions. These intrusions were emplaced in a post-Laramide continental arc setting under shallow conditions, as suggested by fast cooling inferred

from K-Ar biotite ages of ca. 35-33 Ma. Skarn deposits were contemporaneous with emplacement and crystallization of stocks, as revealed by Re-Os molybdenite geochronological data of exoskarn rocks. Skarn rocks show a general depletion of LILE and REE and a slightly enrichment in HFSE in comparison with intrusive rocks. Pyroxene and garnet show dominant hedenbergite and andradite compositions, respectively. The association of hedenbergite, pyrite, chalcopyrite, native bismuth and pyrrhotite during skarn mineralization suggest reducing conditions, typical for Au but not for Cu skarns. Highest metal contents are concentrated in exoskarn rocks, including anomalies of Cu, Fe, Ni, Sn, Sb, Zn, W and Bi. Metal contents, ore minerals and environmental conditions of skarn rocks, together with whole-rock geochemical data of stocks and pyroxene-garnet compositions, reveal some singularities for the Sierra del Fraile deposits, as they exhibit characteristics of both Cu and Au skarn deposits but might be also compatible with Fe, W, and Zn skarns. Hence, skarn and associated vein deposits of the Sierra del Fraile might have a high potential not only for Cu-Au, but also for several base metals, as reported for comparable post-Laramide skarn and hydrothermal deposits of central and northern Mexico.

1. Introduction

Skarns deposits exist in all continents and have been mined for decades because of their large contents of metals. The classification of major skarn deposits is based on their dominant elements, namely Fe, Au, Cu, Zn, W, Mo and Sn (Zharikov, 1970; Einaudi, 1981; Meinert, 1992, Meinert et al., 2005). As most economic skarn deposits are related to magmatic intrusions, the understanding of petrogenesis and tectonic setting of igneous rocks is essential for exploration and classification (Meinert, 1992; Meinert et al., 2005). Additionally, the mineralogical and geochemical data are fundamental for skarn characterization (Einaudi and Burt, 1982; Zharikov et al., 1998; Meinert, 1992), whereas geochronological constraints on both intrusive and associated skarn rocks are critical to assess the timing and duration of ore-forming processes (e.g., Meinert et al., 2005; Chelle-Michou et al., 2015).

Most Mexican Cu and Au deposits are located in western Mexico and comprise a large variety of porphyry-type, skarn, and orogenic deposits, among others, associated with the ca. 80-40 Ma Laramide orogeny (Barton et al., 1995; Albinson and Nelson, 2001; Valencia-Moreno et al., 2006, 2017; Amato et al., 2017; Izaguirre et al., 2017). This orogeny was the result of flat-slab subduction of the Farallón plate beneath the North American plate, and was succeeded by Eocene post-orogenic extension (Dickinson and Snyder, 1978; Clark et al, 1982; Meschede et al., 1997; Bunge and Grand, 2000; Mascuñano et al., 2013; Amato et al., 2017).

The mining district of Santa María de La Paz is located in the Sierra del Fraile, east of Matehuala, in the state of San Luis Potosí, Mexico. This district has been in continuous production for around 150 years and comprises four intrusions and related Cu-(Au) skarn deposits and Ag-Pb-Zn hydrothermal veins, with average grades of 1.3 g/t Au, 150 g/t Ag, 0.9% Cu, 1.8% Zn and 1.1% Pb (Gunnesch et al., 1994; Pinto-Linares, 2008). Pinto-Linares et al. (2008) constrained the age of intrusions at ca. 37-35 Ma, indicating a transitional adakite-like to calc-alkaline geochemical signature.

This work presents new petrographic, mineral and whole-rock geochemical, and geochronological data of intrusions and associated skarns of the Santa María de la Paz mining district, in order to evaluate the petrogenesis of intrusive rocks of the Sierra del Fraile and to characterize skarn deposits and associated ore-forming processes. Further constraints provided by U-Pb LA-ICP-MS zircon ages of intrusive and endoskarn rocks, K-Ar biotite ages of intrusions, and Re-Os molybdenite ages of exoskarns are provided, in order to determine the timing and temporal evolution of intrusions and skarn ore mineralizations.

2. Geological setting

2.1. Regional Geology

The mining district Santa María de la Paz is located at the boundary between two Mesozoic basins, namely the Central Mexico Mesozoic Basin (CMMB) to the west and the Valles–San Luis Potosí Platform (VSLPP) to the east (Fig. 1). The CMMB is constituted by a marine Mesozoic sedimentary sequence of more than 5000 m thickness, with sedimentation beginning in the late Triassic and culminating in the late Cretaceous (Carrillo-Bravo, 1982). The VSLPP consists of Precambrian and Paleozoic metasedimentary rocks, unconformably overlain by Jurassic clastic sediments (Barboza-

Gudiño et al., 2008). Overlaying Precambrian and Jurassic rocks, a Cretaceous marine sequence of evaporites and shallow water limestones occurs, recording a maximum transgression during the Albian-Cenomanian (Carrillo-Bravo, 1982).

The oldest record near the study area are Triassic low-grade metamorphic marine sedimentary rocks (Barboza-Gudiño et al., 1998, 2010; Hoppe et al., 2002), which are unconformably overlain by Lower to Middle Jurassic continental arc deposits of the Nazas Formation or "Nazas Arc" (Pantoja-Alor, 1972; Blickwede, 1981; López-Infanzón, 1986; Barboza-Gudiño et al., 1999, 2008; Bartolini et al., 2003). Marine sedimentation throughout the Mesa Central is recorded from the Oxfordian to the end of Cretaceous. Contemporaneously, more than 4000 m thick, shallow marine carbonate sequences and clastic sediments were accumulated in the VSLPP and CMMB (Carrillo-Bravo, 1982), covering a large portion of the central-eastern Mesa Central between the Late Triassic to Late Cretaceous. Additionally, debris flow and turbiditic deposits are recorded between the western margin of the VSLPP and the transition towards the CMMB (Tamabra Formation; López-Doncel, 2003). All these Mesozoic sequences were strongly deformed during the Laramide orogeny, close to the K/T boundary (Guzmán and de Cserna, 1963; Eguiluz-de Antuñano et al., 2000; Tristán-González et al., 2009). Unconformably, a Paleocene-Eocene sedimentary sequence consisting mostly of red beds or of continental clastic deposits overlays Mesozoic rocks, including intercalations of andesitic lavas (49-44 Ma; Aranda-Gómez and McDowell, 1998; Tristán-González et al., 2009) and covering the VSLPP and CMMB. Bimodal volcanism is recorded afterwards, form the early Oligocene until the early Pliocene.

2.2. Study area

The upper Albian to Cenomanian Cuesta del Cura Formation comprises the oldest exposed unit in the study area, consisting of gray, often laminated limestones interbedded with shales (Fig. 1). The thickness of the Cuesta del Cura Formation ranges between 50 m up to 150 m (Barboza-Gudiño et al., 2004). The Cuesta del Cura Formation is overlapped by the Agua Nueva Formation, which consists of limestones, calcareous marls and siltstones of Turonian age (Barboza-Gudiño et al., 2004), and is stratigraphically overlain by the San Felipe and Méndez formations. The latter two comprise siliciclastic rocks, mainly with micro-clasts of volcanic rocks (Nieto-Samaniego et al., 2007). In the region of La Paz, the maximum thickness of both formations is about 100 meters.

Mesozoic sequences are intruded by four granitic stocks (Membrillo, Santa Teresa, Dolores and Cobriza), resulting in contact metamorphic transformations to skarn or hornfels (Fig. 1). Intrusions yielded discordant U-Pb LA-ICP-MS zircon ages of ca. 37-35 Ma and exhibit a transitional adakite-like to calc-alkaline geochemical signature (Pinto-Linares et al., 2008; Mascuñano et al., 2013). Early mineralization stages are related to the skarn evolution, resulting in Cu-Au-Fe disseminated ore deposits (Gunnesch et al., 1994). This stage is characterized by pyrite, arsenopyrite, chalcopyrite, native bismuth and pyrrhotite as main ore minerals, and was succeeded by polymetallic Ag-Pb-Zn vein deposits (Gunnesch et al., 1994). The entire area is cross-cut by N-S extensional normal faults of the Taxco-San Miguel de Allende fault system, which controlled the emplacement of the La Paz Dyke System and associated hydrothermal Ag-Pb-Zn deposits (Castro-Larragoitia, 1990).

3. Methodology

3.1. Petrography and whole-rock geochemistry

Petrographic and whole-rock geochemical analysis were carried out in 27 samples of intrusive and skarn rocks, mostly obtained from underground drilling cores. Fifteen intrusive samples were collected, whereas twelve samples were obtained from the skarn. Major elements were measured with a PANanalytical Axios Advanced wavelength dispersive XRF spectroscope at the GeoForschungsZentrum Potsdam (GFZ). Crushed and dried samples were melted down to tablets with lithium tetraborate metaborate (Fluxana FX-X65), with a sample to flux ratio of 1:6. The H_2O and CO_2 contents were determined with a Vario EL III (Elementar Analysensysteme GmbH, Hanau). The determination of the sulfur content was carried out by an ELTRA CS 200 (ELTRA GmbH, Neuss). Trace element analyses were performed at the Geoscience Center of the Georg-August-Universität Göttingen with a Perkin Elmer DRC II Inductively Coupled Mass Spectrometer (ICP-MS). Analyses were validated by repeated independent sample preparation, blanks and analyses of two different international reference standards. Results were analysed using the GCDkit 4.1 software (Janoušek et al., 2006, 2016).

3.2. Mineral chemistry

Thin sections were prepared and analyzed in the microprobe laboratory of the Geoscience Center of the Georg-August-Universität Göttingen. Thin sections were polished in two steps (3 und 1 µm) and vaporized with carbon. Measurements were carried out with a JEOL JXA 8900 RL wavelength dispersive electron microprobe in the microprobe laboratory at the GZG. Measurements allow a spot resolution of 1-2 µm and a detection limit of < 30 ppm. All elements with an atomic number $Z \geq 5$ can be measured.

3.3. Geochronology

3.3.1. U-Pb LA-ICP MS

U-Pb zircons ages were obtained for four intrusive rocks and two endoskarn samples at Stellenbosch University in South Africa. Samples were crushed and sieved and, afterwards, the mineral fractions were separated using conventional heavy liquid and isodynamic techniques. Zircon U-Pb dating was done with a Single Collector–Magnetic Sectorfield–Inductively Coupled Plasma–Mass Spectrometer (LA-SF-ICP-MS). A Resonetics Resolution S155 Excimer Laser in combination with a Finnigan Element 2 Mass Spectrometer was used. Detailed description of the methods for analysis and evaluation of the measurements can be found in Gerdes and Zeh (2006) and Frei and Gerdes (2009). Measurements were verified by using Plešovice (Sláma et al., 2008) and M127 (Nasdala et al., 2008; Mattinson, 2010) as standard zircon reference material. The calculation of concordia ages and concordia plots were carried out with the programme Isoplot 3.0 (Ludwig, 2003).

3.3.2. K-Ar

K-Ar biotite ages were determined in eight samples of intrusive rocks at the Geoscience Center of the Georg-August-Universität Göttingen. Samples were crushed and sieved in different grain size fractions depending on the size of the biotites. The biotite minerals were separated by standard techniques like magnetic separation and hand picking. The purity of the biotite separates was >99%. Purified biotites were ground in pure alcohol to remove altered rims that might have suffered a loss of Ar or K.

The argon isotopic composition was measured in a pyrex glass extraction and purification line coupled to a Thermo Scientific ARGUS VI noble gas mass spectrometer operating in static mode at the Geoscience Centre of the Georg–August–Universität Göttingen. The amount of radiogenic [40]Ar was determined by isotope dilution method using a highly enriched [38]Ar spike from Schumacher (1975). The spike is calibrated against the biotite standard HD-B1 (Fuhrmann et al., 1987). The age calculations are based on the constants recommended by the IUGS quoted in Steiger and Jäger (1977).

Potassium was determined in duplicate by flame photometry using a BWB-XP flame photometer. The samples were dissolved in a mixture of HF and HNO_3 according to the technique of Heinrichs and Herrmann (1990). The analytical error for the K/Ar age calculations is given on a 95% confidence level (2σ). Details of argon and potassium analyses for the laboratory in Göttingen are given in Wemmer (1991).

3.3.3. Re-Os

The Re-Os age was obtained in one molybdenite sample from the exoskarn of the Cobriza intrusion. For the Re measurement, the sample was cleaned chromatographically with TEVA Harz (Fa. Triskem) and measured with LA-ICP-MS, in alternation with the standard ARM 2007 (Markey et al., 2007). On the other hand, determination of [187]Os was performed with a Finnigan MAT 261 NTI-MS (Negative Thermal Ionization Mass Spectrometer), alternating sample and standard. The Re-Os age was calculated considering a [187]Re decay constant of $1.666 \times 10^{-11}\,a^{-1}$ (Smoliar et al., 1996). For further details of sample preparation and analytical procedures, see Völkening et al. (1991), Walczyk et al. (1991) and Brauns (2001).

4. Results

4.1. Field observations and petrography

4.1.1. Intrusive rocks

All four intrusions of the Sierra del Fraile are porphyritic leucocratic igneous bodies that show holocrystalline, heterogranular textures. The groundmass consists of quartz and K-feldspar, whereas phenocrysts are hypidiomorphic to idiomorphic plagioclase (35-40%), xenomorphic quartz (20-25%), hypidiomorphic to xenomorphic K-feldspar (25-30%) and mafic minerals (biotite and hornblende, 10-15%). Plagioclase

phenocrysts show zoning and typical polysynthetic twins. Accessories are zircon, apatite and titanite/sphene.

The composition of the Membrillo, Santa Teresa and Dolores stocks is monzogranitic. In the Membrillo intrusion, plagioclase and biotite show alteration to sericite and chlorite, respectively. The Santa Teresa intrusion is cross-cut by a variety of mineralized veins, mostly filled with calcite, pyrite and chalcopyrite. Biotite shows slightly chloritisation. In the case of the Dolores intrusion, alteration of plagioclase, biotite and hornblende crystals increase from the centre to the rim of the pluton. At the rim of this igneous body, fractures mineralized with calcite and secondary formed pyrite can be observed. On the other hand, the Cobriza intrusion shows a monzogranitic to granodioritic composition. Like the samples from the Dolores intrusion, the alteration of the minerals increases from the centre to the rim of the intrusion. Calcite-mineralized fractures at the rim of the intrusion and secondary pyrite can be also observed.

4.1.2. Endoskarn

Endoskarns were only formed at the rim of the Dolores and Cobriza intrusions, showing thicknesses of up to 5 and 10 m, respectively. Excepting for scarce relics, the primary magmatic texture is no longer observable. Both at macro- and microscopic scale, endoskarns are medium-grained and equigranular to heterogranular. The composition of the endoskarn is highly variable and changes with the distance to the intrusion, which can be macroscopically noticed by a color change. It ranges from red, where garnet is the main mineral, to greenish gray, where pyroxene is the main mineral (Fig. 2a, b). The pyroxene content increases with the increasing distance to the intrusion, while the garnet content decreases.

Garnet, pyroxene and sulfides are the main minerals of the endoskarns. In thin section, hypidiomorphic to xenomorphic garnets are slightly reddish and present an average grain size of 0.25 mm. Xenomorphic pyroxene crystals with an average grain size of 0.4 mm are typically observed between garnets. Main sulphides are pyrite and subordinated chalcopyrite, which are mostly idiomorphic. The grain size of sulphides vary from ca. 0.1 mm to 3 mm. Carbonates are observable as well, occurring preferentially in veinlets (Fig. 2b). Though scarce, relic plagioclase and quartz crystals of the intrusion are present as well. Plagioclase alteration increases towards the wall-rock,

being incipient at the intrusion-endoskarn contact and profuse at the endoskarn-exoskarn contact.

4.1.3. Exoskarn

Macroscopically, exoskarn rocks are massive and fine-grained. The composition varies with increasing distance to the pluton, showing a garnet content decrease and a pyroxene content increase. Further away from the intrusion, the pyroxene content decreases again and the wollastonite content rises. Hence, colors range from red, where garnet is the mainly occurring mineral (Fig. 2c), over green-gray, with predominantly pyroxene composition, to white up to gray, where wollastonite is the dominant mineral. The sedimentary lamination is mostly overprinted and only locally observed (Fig. 2d).

At the microscopic scale, xenomorphic garnets show a variable grain size that decreases with increasing distance to the intrusion, reaching a maximum average of 0.5 mm close to the contact. Pyroxenes have a xenomorphic shape and an average grain size of approximately 0.4 mm. Samples of the outermost edge of the exoskarns show a retrograde mineral association with actinolite-tremolite. Large accumulations of sulphide ores can be found in the exoskarns, including pyrite, bornite, chalcopyrite, molybdenite, sphalerite and subordinated arsenopyrite (Fig. 2e, f). Also, carbonates are relic or filling of cavities.

4.2. Mineral chemistry

4.2.1. Intrusive rocks

Plagioclase crystals show an average composition of andesine in the Dolores (anorthite (An) = 37.70%, albite (Ab) = 60.19%, and orthoclase (Or) = 2.11%) and Cobriza intrusions (An = 35.32%, Ab = 62.36%, and Or = 2.32%) (Fig. 3). In both cases, only few analysis show oligoclase or labradorite compositions. Significant changes in composition perpendicular to the zonation were not observed. On the other hand, analyses of plagioclases from the Cobriza endoskarn and a fine-grained enclave of the Cobriza stock show similar andesine compositions (Fig. 3).

4.2.2. Endoskarn

Microprobe analyses were performed to determine the end-member composition of plagioclase, garnet and pyroxenes. Only fresh plagioclases of the Cobriza endoskarn

were analyzed, showing an average andesine composition (An = 39.59%, Ab = 59.05%, and Or = 1.36%) similar to plagioclases in the Cobriza monzogranite (Fig. 3). For pyroxenes, an average hedenbergite composition was obtained for samples of the Dolores endoskarn and exoskarn, and the Cobriza endoskarn (Fig. 4). As the Zn content was not measured, the determination of the end-member petedunnite ($CaZnSi_2O_6$) could not be evaluated. Therefore, only a distinction of Ca pyroxene between hedenbergite, diopside and johannsenite was possible. Finally, garnets of the Dolores endoskarn exhibit an average composition of andradite = 90.86%, grossular = 7.94%, uvarovite = 0.07% and pyralspite group = 1.14% (Fig. 5).

4.2.3. Exoskarn

Garnet and pyroxene compositions were determined for samples of the Dolores and Cobriza exoskarns. In the Dolores exoskarn, pyroxenes show a hedenbergite composition, similarly to the respective endoskarn. Hedenbergites of exoskarn, however, have a slightly higher Fe content (Fig. 4). Garnets have an almost identical composition to the endoskarn (andradite = 90.43%, grossular = 8.43%, uvarovite = 0.09% and pyralspite group = 1.14%), with a predominantly andraditic composition (Fig. 5). On the other hand, garnets of the Cobriza exoskarn show an average composition of andradite = 76.1%, grossular = 22.5%, uvarovite = 0.1% and pyralspite = 0.8% (Fig. 5), being thus slightly more enriched in Al and more depleted in Fe than garnets of the Dolores exoskarn.

4.3. Whole-rock geochemistry

Analytical results are displayed in Appendix 1. Data processing and plots were carried out using using GCDkit 4.1 (Janoušek et al., 2006, 2016), including results from intrusions reported by Pinto-Linares et al. (2008).

4.3.1. Intrusive rocks

Intrusions show a relatively narrow range of SiO_2 content, varying between ca. 63 and 68 wt. %, though three samples of the Dolores intrusion show slightly higher values of around 72 wt. % (Table 1; Pinto-Linares et al., 2008). All samples show compositions that vary between granitic to granodioritic (Fig. 6a; Cox et al., 1979) and dominantly metaluminous to slightly peraluminous (Fig. 6b; Shand, 1943). Based on criteria of Frost

et al. (2001), the Sierra del Fraile stocks show dominant magnesian (Fig. 6c) and calc-alkalic compositions (Fig. 6d). Likewise, they mostly correspond to the high-K calc-alkaline series, with a slight tendence towards the shoshonite series (Peccerillo and Taylor, 1976).

Trace element patterns display a general steep negative slope in the primitive mantle-normalized plot, with marked negative anomalies of Nb-(Ta), P and Ti and positive anomalies of U and Pb (Fig. 7a) and enrichment in LILE with respect to HFSE. On the other hand, chondrite-normalized REE patterns show an enrichment in LREE with respect to HREE (Fig. 7b). A slightly to well-developed negative Eu anomaly is present in all samples (Fig. 7b), with Eu_N/Eu_N^* between 0.36 and 0.84 (Table 1), suggesting plagioclase fractionation. Moderate REE fractionation patterns are evident for most samples (Fig. 7b, Table 1), being slightly higher for those of the Cobriza intrusion (25.14 ≤ La_N/Yb_N ≤ 43.27; Table 1).

4.3.2. Skarn

Trace elements of both endoskarn and exoskarn rocks show a general depletion of LILE (K, Rb, Ba, Sr) and slightly enrichment in HFSE in comparison with intrusive rocks (Table 1, 2; Fig. 8a). Chondrite-normalized REE patterns show a general depletion of REE in skarn samples (Fig. 8b), though REE fractionation is comparable in skarn and intrusive rocks (2.25 ≤ La_N/Yb_N ≤ 43.36; Table 2).

If compared, Cu concentration increases from intrusive to exoskarn rocks (Fig. 9). A similar pattern is observed for other metals such as Fe, Ni, Sn, Sb, Zn, W and Bi (Table 1, 2), indicating that ore mineralizations are clearly concentrated in skarn, particularly exoskarn rocks.

4.4. Geochronology

4.4.1. U-Pb LA-ICP-MS

In all samples, cathodoluminescence images show zircons that are dominantly prismatic and exhibit oscillatory zoning, pointing to a magmatic origin (Fig. 10). Cores showing oscillatory or sector zoning are locally observed as well.

Concordant crystallization ages within the range of ca. 37.6-35.0 Ma were obtained for all samples, which also present zircon xenocrysts yielding Tonian, Devonian-Carboniferous and Cretaceous ages (Fig. 11, Appendix 1). Ages of 37.3 ± 0.3

and 36.8 ± 0.3 Ma were calculated for samples MGA and DQ76GD of the Membrillo and Santa Teresa stocks (Fig. 11a, 11b), respectively. Both the western Dolores intrusion (sample DJ14GR-2) and associated endoskarn (sample DO48SR-2) present comparable ages of 36.3 ± 0.3 and 36.2 ± 0.3 Ma (Fig. 11c, 11d), respectively. Likewise, zircons of the northwestern Cobriza intrusion (sample CO23-30GC) yield an age of 35.7 ± 0.3 Ma (Fig. 11e), similarly to the Cobriza endoskarn age of 35.3 ± 0.3 Ma (CO7801-20ENS) (Fig. 11f).

4.4.2. K-Ar

Results of K-Ar biotite ages for samples of the Santa Teresa, Dolores, and Cobriza intrusions are shown in Table 3. Due to extreme alteration, reliable biotite K-Ar ages for the Membrillo intrusion were not obtained. For the Santa Teresa intrusion, an age of 35.05 ± 0.89 Ma was determined. Ages of 35.43 ± 0.45 and 30.92 ± 0.41 Ma were obtained for the eastern Dolores intrusion, whereas an age of 35.07 ± 0.55 Ma was calculated for a sample of the eastern part. In the northwestern Cobriza stock, biotites yield two comparable ages of 34.23 ± 0.60 and 34.06 ± 0.59 Ma. Similarly, ages of 33.80 ± 0.36 and 27.13 ± 0.41 Ma were determined for the southeastern Cobriza stock.

4.4.3. Re-Os

Analytical results of Re-Os dating in molybdenites of the Cobriza exoskarn are presented in Table 4. An average molybdenite Re-Os age of 38.07 ± 0.27 Ma was obtained, being thus comparable with U-Pb ages obtained for the intrusions (Fig. 11).

5. Discussion

5.1. Petrogenesis of the Santa María de la Paz district magmatism

Worldwide, most significant Cu skarns are associated with Cu mineralized porphyries (Meinert et al., 2005). In Mexico, economically important Cu porphyry deposits were emplaced between the Upper Cretaceous and the Eocene, being intimately related to the Laramide Orogeny (Barton et al., 1995; Valencia-Moreno et al., 2017; Centeno-García, 2017). Intrusions and associated skarn deposits in the Sierra del Fraile, however, are younger and were interpreted as the result of the post-orogenic Laramide phase (Pinto-Linares et al., 2008; Mascuñano et al., 2013). Additionally, Pinto-Linares et al. (2008) indicated a transitional adakite-like to calc-alkaline geochemical signature for

the Sierra del Fraile magmatism, whereas Mascuñano et al. (2013) interpreted an affinity with high Ba-Sr granitoids.

Petrographic and whole-rock geochemical data (Section 4.1.1, 4.3) indicate that stocks of the Sierra del Fraile comprise granites and granodiorites with dominant metaluminous to slightly peraluminous, magnesian and calc-alkalic compositions, typical of Cordilleran granites (Frost et al., 2001). High-K calc-alkaline compositions (Peccerillo and Taylor, 1976) and negative Nb-(Ta), P and Ti anomalies further support a continental arc affinity.

Key features of both adakite and high Ba-Sr magmatism are the lack of Eu anomaly, high Sr/Y and La_N/Yb_N, and very low Y and Yb contents (Drummond and Defant, 1990; Martin, 1999; Fowler et al., 2001; Richards and Kerrich, 2007; Gómez et al., 2015; Lara et al., 2017). In contrast, most samples of the Sierra del Fraile intrusions show a negative Eu anomaly, whereas Sr/Y and La_N/Yb_N ratios, and Y and Yb contents are more similar to those recorded by normal arc rocks (Table 1, Fig. 12). Additionally, comparison with experimental data of Patiño Douce (1999) suggests an origin related to partial melting of mafic rocks and subordinated immature sediments (Fig. 13). The latter might account for zircon xenocrysts yielding variable Tonian to Cretaceous ages (Appendix 1).

Structural and geochronological data constrain the timing of the Laramide Orogeny at ca. 60 Ma for the study area (Tristán-González et al., 2009; Cuéllar-Cárdenas et al., 2012), thus supporting a post-Laramide setting for the Santa María de la Paz district magmatism, as previously indicated (Pinto-Linares et al., 2008; Mascuñano et al., 2013). Further Paleogene post-Laramide mineralizations are recorded in the region, constituting essentially skarn and epithermal deposits. Ag-Pb-Zn-Au veins in the Sierra de Catorce, immediately west of the Sierra del Fraile, are associated with granitoids yielding U-Pb zircon ages of ca. 45-40 Ma (Mascuñano et al., 2013). Contemporaneous magmatism and related Zn-Cu skarn mineralizations yielding a K-Ar orthoclase age of 43 ± 3 Ma were reported in the Charcas district (Mujica-Mondragón and Jacobo-Albarrán, 1983). Further west, Re-Os molybdenite ages of ca. 44-43 Ma constrain the timing of Zn-Pb-Cu-(Ag)±(Au) skarn and epithermal deposits of the San Martín district in the central Sierra Madre Occidental (Camprubí et al., 2015). In the Taxco district of the Sierra Madre del Sur, maximum U-Pb zircon and $^{40}Ar/^{39}Ar$ K-feldspar ages of ca. 35 Ma were obtained for Ag-Zn-Pb intermediate sulfidation epithermal deposits (Farfán-Panamá et al., 2015), thus being probably contemporaneous with the La Azul fluorite deposit, which presents

(U-Th)/He fluorite ages of ca. 33-30 Ma (Pi et al., 2005). Oligocene K-Ar whole-rock ages of ca. 31-29 Ma were also reported for intrusion-related mineralizations of the Fresnillo silver district in Zacatecas, southwest of San Luis Potosí (Lang et al., 1988).

Tectonic discrimination diagrams based on geochemical data are not conclusive, despite suggesting a possible continental arc setting (Fig. 14). It is thus argued that post-Laramide intrusions did not result from processes linked to the genesis of adakitic magmas or high Ba-Sr granitoids but, instead, from partial melting of mafic and subordinated Al-poor sediments that led to high-K calc-alkaline magmatism, typical of Cordilleran magmatism related to convergent settings (Patiño Douce, 1999; Frost et al., 2001). Though unclear, a possible mechanism for the genesis of the Santa María de la Paz district magmatism might imply post-Laramide slab removal of the Farallon slab that led to low-volume partial melting of a hydrated and fertile lithospheric mantle, which resulted from metasomatism during Laramide flat-slab subduction (Fig. 15; Humphreys, 1995, 2009; Ferrari et al., 1999, 2017). During ascent, magmas might also incorporate crustal rocks, as evidenced by zircon inheritance. Ferrari et al. (2017) indicated this mechanism as the most likely explanation for the middle to late Eocene magmatism of northeastern Mexico, thus accounting for the ca. 45-35 Ma post-Laramide magmatism and associated mineralizations of the region.

5.2. Skarn evolution and ore-forming processes

5.2.1. Temporal constraints

One of the most critical points to understand the genesis of ore deposits, particularly those related to skarns, is to provide robust temporal constraints, which essentially means to assess the timing and duration of ore-forming processes (e.g., Meinert et al., 2005; Chelle-Michou et al., 2015). Therefore, geochronological constraints on both skarn and intrusive rocks are required (Porter and Selby, 2010; Li et al., 2014; Chelle-Michou et al., 2015; Deng et al., 2015).

U-Pb LA-ICP-MS zircons ages obtained in stocks of the Sierra del Fraile are within the range of ca. 37.6-35.0 Ma (Section 4.1.1), being thus equivalent to previous geochronological constraints on these intrusions (Pinto-Linares et al., 2008; Mascuñano et al., 2013). Though slightly older, the Re-Os molybdenite age of 38.07 ± 0.27 Ma obtained for the Cobriza exoskarn is comparable to crystallization ages of the plutons, indicating the magma emplacement, skarn metasomatism and ore mineralization were

simultaneous (Zharikov, 1970), as recorded in other skarn deposits (Li et al., 2014; Chelle-Michou et al., 2015; Deng et al., 2015). During magma emplacement, skarn metasomatism triggered by fluid circulation might be slightly older than magma crystallization, thus accounting for the slightly differences between Re-Os molybdenite and U-Pb zircon ages.

On the other hand, closure temperatures for Re-Os in molybdenite and K-Ar in biotite were estimated at ca. 500°C and 350-300°C, respectively (Harrison et al., 1985 Grove and Harrison, 1996; Suzuki, 1996). The Re-Os age of the Cobriza exoskarn is more or less equivalent to zircon ages obtained in the Cobriza stock, whereas K-Ar biotite ages are slightly younger than their respective U-Pb zircon ages, showing differences of less than ca. 2 m.y. in most cases (Section 4.4). Only one K-Ar age of 27.13 ± 0.41 Ma is considerably younger and might result from partial Ar loss, as a second age of 33.80 ± 0.36 Ma was obtained for the same part of the pluton. Assuming a crystallization temperature of ca. 750-700°C for the intrusions and a closure temperature of ca. 360-380°C for Ar diffusion in biotites with an effective diffusive radius of 500 μm (Harrison et al., 1985; Grove and Harrison, 1996), cooling rates of ca. 0.2-0.3°C/k.y. can be estimated. Results thus point to a very fast cooling of intrusions, indicating shallow emplacement conditions.

5.2.2. Skarn characterization and ore deposition

Skarn-related magmatic rocks provide not only information to classify skarn deposits but also to characterize their genetic conditions (Meinert, 1992; Meinert et al., 2005). Geochronological data of the Santa María de la Paz district point to a shallow setting (Section 5.2.1), further supported by fluid inclusion data (Gunnesch et al., 1994), which is typical of Cu skarn deposits (Meinert, 1992; Meinert et al., 2005). On the other hand, geochemical data of stocks point to crustal high-K calc-alkaline magmas as the main source of mineralizations. The crustal fingerprint of magmas is also indicated by zircon inheritance (Appendix 1) and low Re contents in molybdenite (Table 4; Mao et al., 1999).

Skarn rocks of the Sierra del Fraile are quite different in their mineral composition (Section 4.1), showing a general zonation of five different mineral aggregate zones moving from the intrusion to the carbonate rocks:

1. Plagioclase- and quartz-rich zone with increasing alteration. Increasing amount of garnets and subordinated pyroxenes (endoskarn).

2. Garnet zone with continuous increasing amount of garnet (first exoskarn area).

3. Pyroxene zone with increasing amount of wollastonite and minor amount of garnets.

4. Wollastonite zone next to the carbonates with minor amount of garnet and pyroxene.

5. Marble or hornfels zone, depending on the wall-rock (limestone and shale, respectively).

Though pyroxene and garnet show significant variations in their relative abundances and grain size (Section 4.1), no significant changes are observed in their compositions (Fig. 3, 4). Hedenbergite and andradite compositions are dominant, as previously indicated for the Dolores skarn (Gunnesch et al., 1994), showing a slightly increase of Mg/Fe and Al/Fe, respectively, from the endoskarn to the exoskarn (Fig. 3, 4). The association of hedenbergite + pyrite together with the presence of pyrrhotite and the lack of magnetite-hematite (Gunnesch et al., 1994) suggest reducing and variable sulfidizing conditions, based on comparison with experimental data at 2 kbar and 300-600°C for the Ca-Si-Fe-O-S system (Burton et al., 1982; Gamble, 1982). Further evidence of low fO_2 is provided by the presence of sulfide-rich mineralizations with pyrite + chalcopyrite + native bismuth + pyrrhotite, resembling characteristics of reduced Au-Cu-Bi iron oxide deposits of the Tennant Creek Inlier, Australia (Skirrow and Walshe, 2002).

If compared with other Cu-Au skarns, skarns of the Sierra del Fraile show some singularities. Inferred reducing conditions are expected for gold but not for copper skarns, as the latter are typically more oxidized (Meinert et al., 2005). Pyroxene compositions are comparable to those of Au, Fe and W skarns, whereas garnets show compositions compatible with most skarn types (Einaudi and Burt, 1982; Meinert, 1992). Concerning Cu skarns, the main difference is the presence of hedenbergitic pyroxene, contrasting with typical diopside-dominated compositions (e.g.; Einaudi and Burt, 1982; Meinert, 1992). Andradite- and hedenbergite-dominated compositions were reported for the Changlongshan iron skarn of China (Xu and Lin, 2000) and tungsten skarn deposits of the Taebaeksan mineral district, South Korea (Park et al., 2017). On the other hand, Ni, V, Sc, Rb, Rb/Sr and Zr contents of the Sierra del Fraile intrusions

(Appendix 1) are similar to mean values of plutonic rocks associated with Cu skarns, though some parameters are also comparable to those of Zn, Au and Fe skarns (Meinert, 1995; Meinert et al., 2005).

Together with Cu and Au, for which the Sierra del Fraile skarns are exploited, high contents of other metals such as Fe, Ni, Sn, Sb, Zn, W and Bi are evident in skarn, particularly exoskarn rocks (Table 1, 2). Cu and Fe mineralizations are mainly related to phyrite, chalcopyrite and phyrrotite, whereas Au is mainly contained in arsenopyrite and in minor amounts of Au tellurides (krennerite) (Gunnesch et al., 1994). However, Au is also associated with native bismuth (Gunnesch et al., 1994), which can be explained based on the capacity of Bi-melts to scavenge Au (Tooth et al., 2008, 2011). High Sb contents were also reported for the Sierra de Catorce (Tuta et al., 1988) and, together with Ag-Pb-Zn mineralizations, are mainly related to late vein deposits (Gunnesch et al., 1994). The presence of sphalerite would account for the high Zn contents. Though W and Sn contents cannot be easily explained by data, Paleocene-Eocene tungsten and Oligocene tin deposits, respectively, are common in central Mexico (Mead et al., 1988; Tuta et al., 1988).

Skarn deposits of the Sierra del Fraile have been typically considered as Cu-(Au) skarns (Gunnesch et al., 1994; Pinto-Linares et al., 2008), though they show some singularities, in terms such as their significant content in several base metals. Likewise, pyroxene and garnet skarn compositions and whole-rock geochemical data of related intrusions show some similarities with other Cu skarn deposits (Einaudi and Burt, 1982; Meinert, 1992, 1995; Meinert et al., 2005), though compositions show also an affinity with Au, Fe and Zn skarn types.

6. Conclusions

U-Pb LA-ICP-MS zircon data indicate crystallization ages of ca. 37.6-35.0 Ma for skarn-related stocks of the Sierra del Fraile. These granitic to granodioritic intrusions show dominant metaluminous to slightly peraluminous, high-K calc-alkaline compositions, resulting from magmas that were emplaced in a post-Laramide continental arc setting. Fast cooling rates of ca. 0.2-0.3°C/k.y. are estimated based on K-Ar biotite ages of ca. 35-33 Ma, which might indicate shallow emplacement conditions.

Skarn deposits were contemporaneous with emplacement and crystallization of stocks, as revealed by Re-Os molybdenite geochronological data of exoskarn rocks. Skarn rocks show a general depletion of LILE and REE and a slightly enrichment in HFSE in comparison with intrusive rocks. Pyroxene and garnet show dominant hedenbergite and andradite compositions, respectively. The association of hedenbergite, pyrite, chalcopyrite, native bismuth and pyrrhotite during skarn mineralization suggest reducing conditions, which are expected for Au but not for Cu skarns. Highest metal contents are restricted to skarn, particularly exoskarn rocks, including anomalies of Cu, Fe, Ni, Sn, Sb, Zn, W and Bi.

Comparison with other skarn deposits reveal some singularities for skarns of the Sierra del Fraile. Metal contents, ore minerals and environmental conditions, together with whole-rock geochemical data of stocks and pyroxene-garnet compositions, show similarities with both Cu and Au skarn deposits, despite of being also compatible with Fe, W, and Zn skarns. Hence, skarn and associated vein deposits of the Sierra del Fraile might have a high potential not only for Cu-(Au) but also for several base metals, as reported for comparable post-Laramide skarn and hydrothermal deposits of central and northern Mexico.

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Fig. 1. Geological map of the Santa María de la Paz district in the Sierra de Fraile.

Fig. 2. Representative drill core (a-d), hand specimen (e) and thin section (f) samples of Sierra del Fraile skarn rocks. a) Dolores endoskarn, showing altered remnants of the intrusion (lower part), pyroxene and disseminated pyrite. b) Cobriza endoskarn, mostly dominated by pyroxene and late calcite veinlets. c). Dolores exoskarn, consisting mostly of garnet and subordinated pyroxene. d). Dolores exoskarn close to the wall rock, showing garnet replacement (upper part) and relics of the primary bedding in limestone (lower part). e). Ore-bearing Cobriza skarn made up of pyrite, bornite and subordinated arsenopyrite. f) Photomicrograph (reflected light) of ore minerals in the Dolores exoskarn. Py: pyrite, Px: pyroxene, Cal: calcite, Grt: garnet, Apy: arsenopyrite, Bn: bornite.

Fig. 3. Ternary classification of feldspars of intrusion (Dolores and Cobriza) and endoskarn samples (Cobriza).

Fig. 4. Classification of pyroxenes from different skarn samples in a) the quaternary Ca-Fe-Mg-system after Morimoto (1988) and b) ternary Ca-system.

Fig. 5. Classification of garnets from different skarn samples in the ternary Ca-garnet-pyralspite-system.

Fig. 6. Major element results for the Sierra del Fraile intrusive rocks of this study (circles) and Pinto-Linares et al. (2008) (triangles). Dolores intrusion: red, Cobriza intrusion: yellow, Membrillo intrusion: light blue, Santa Teresa intrusion: blue. a) TAS classification diagram after Cox et al. (1979). Alkaline and subalkaline/tholeiitic fields after Miyashiro (1978). The circles represent the data of this work and the squares of the previous work by Pinto-Linares et al. (2008). b) A/CNK vs A/NK plot after Shand (1943). c) SiO_2 vs Fe* index = $FeO_t/(FeO_t + MgO)$ after Frost et al. (2001). d) SiO_2 vs MALI index = $Na_2O + K_2O - CaO$ after Frost et al. (2001). e) K_2O vs. SiO_2 diagram after Peccerillo and Taylor (1976).

Fig. 7. Trace element results for the Sierra del Fraile intrusive rocks of this study (circles) and Pinto-Linares et al. (2008) (triangles). Dolores intrusion: red, Cobriza intrusion: yellow, Membrillo intrusion: light blue, Santa Teresa intrusion: blue. a) Primitive mantle-normalized multielement plot (primitive mantle composition after

McDonough and Sun, 1995). b) Chondrite-normalized REE plot (chondrite composition after Boynton, 1984).

Fig. 8. Trace element results for the Sierra del Fraile endoskarn (x) and exoskarn (+) rocks. Grey areas indicate composition of intrusive rocks of Fig. 6. Dolores intrusion: red, Cobriza intrusion: yellow, Santa Teresa intrusion: blue. a) Primitive mantle-normalized multielement plot (primitive mantle composition after McDonough and Sun, 1995). b) Chondrite-normalized REE plot (chondrite composition after Boynton, 1984).

Fig. 9. Boxplot of Cu contents (ppm) for intrusive, endoskarn and exoskarn rocks of the Sierra del Fraile. Note that $[Cu]_{intrusions} < [Cu]_{endoskarn} < [Cu]_{exoskarn}$.

Fig. 10. Cathodoluminescence images of representative zircons with individual $^{206}Pb/^{238}U$ ages and respective 2σ errors (sample CO23-30GC).

Fig. 11. U-Pb diagrams. Red and green ellipses indicate data used for age calculations and concordia age, respectively. Errors depicted at the 2σ level. Analytical data are presented in Appendix 1.

Fig. 12. Y vs Sr/Y diagram showing fields for arc calc-alkaline and adakite-like rocks after Drummond and Defant (1990). Circles: this study, triangles: Pinto-Linares et al. (2008). Dolores intrusion: red, Cobriza intrusion: yellow, Membrillo intrusion: light blue, Santa Teresa intrusion: blue.

Fig. 13. $Al_2O_3 + Fe_2O_3 + MgO + TiO_2$ vs $Al_2O_3 / (Fe_2O_3 + MgO + TiO_2)$ diagram showing compositions of intrusions of the Sierra del Fraile, including fields of melt compositions experimentally generated by melting of various lithologies after Patiño-Douce (1999). Circles: this study, triangles: Pinto-Linares et al. (2008). Dolores intrusion: red, Cobriza intrusion: yellow, Membrillo intrusion: light blue, Santa Teresa intrusion: blue.

Fig. 14. Tectonic discrimination diagrams based on geochemical data. Circles: this study, triangles: Pinto-Linares et al. (2008). Dolores intrusion: red, Cobriza intrusion: yellow, Membrillo intrusion: light blue, Santa Teresa intrusion: blue. a) Y + Nb vs Rb diagram after Pearce et al. (1984). b) R_1 vs R_2 diagram after Batchelor and Bowden (1985).

Fig. 15. Tectonic and geodynamic scenario for petrogenesis of the Sierra del Fraile magmatism (modified after Ferrari et al., 2017), showing schematically the most likely setting for the genesis of the Santa María de la Paz district magmatism. Post-Laramide slab removal of the Farallon slab led to low-volume partial melting of a hydrated and fertile lithospheric mantle, which resulted from previous metasomatism during Laramide flat-slab subduction (Humphreys, 1995, 2009; Ferrari et al., 1999, 2017). See Section 5.1 for further discussion.

Table 1. Results of major and trace element analyses of intrusive rocks in the Sierra del Fraile. Eu*=$\sqrt{Sm_N \times Gd_N}$. Chondrite-normalized values after Boynton (1984).

Table 2. Results of major and trace element analyses of skarn rocks in the Sierra del Fraile. Eu*=$\sqrt{Sm_N \times Gd_N}$. Chondrite-normalized values after Boynton (1984).

Table 3. Results of K-Ar age determinations in biotites of intrusive rocks.

Table 4. Results of the Re-Os age determination (± 2σ) in molydonites of the Cobriza exoskarn. Age determinations of the ARM 2007 standard (Markey et al., 2007) are presented as well.

Legend

Quaternary	
Alluvium	
Basalt	
Paleogene	
Hornfels-Skarn	
Plutonic Rocks	
Cretaceous	
Méndez Fm.	
San Felipe Fm.	
Agua Nueva Fm.	
Cuesta del Cura Fm.	

Village/Town

===== Paved road

Mine

Altitude

Fault

CMMB Central Mexico Mezosoic Basin

VSLPP Valles-San Luis Potosí Platform

Study area

Or
(KAlSi$_3$O$_8$)

Legend:
- E Dolores
- NW Cobriza
- NW Cobriza enclave
- NW Cobriza endoskarn

Alkali feldspars

Sanidine

Anorthoclase

miscibility gab

Albite

Oligoclase

Andesine

Labradorite

Bytowinite

Anorthite

Plagioclase feldspars

Al
(NaAlSi$_3$O$_8$)

An
(CaAl$_2$Si$_2$O$_8$)

Legend:
- Dolores W exoskarn
- Dolores E endoskarn
- Cobriza NW exoskarn

Pyralspites

Grossular
$Ca_3Al_2[SiO_4]_3$

Andradite
$Ca_3Fe_2[SiO_4]_3$

Cobriza NW

30 GC_04
35.0 ± 1.0 Ma

30 GC_11
36.6 ± 1.1 Ma

30 GC_03
36.3 ± 1.0 Ma

30 GC_17
36.3 ± 1.1 Ma

30 GC_02
36.0 ± 1.1 Ma

100 μm

a Membrillo Intrusion

MGA
Concordia Age = 37.3±0.3 Ma
(2σ, decay-const. errs ignored)
MSWD (of conc. & equiv.) = 0.70,
Probability (of conc. & equiv.) = 0.85

b Santa Teresa Intrusion

DQ76GD
Concordia Age = 36.8±0.3 Ma
(2σ, decay-const. errs ignored)
MSWD (of conc. & equiv.) = 1.3,
Probability (of conc. & equiv.) = 0.17

c W Dolores Intrusion

DJ14GR-2
Concordia Age = 36.3±0.3 Ma
(2σ, decay-const. errs ignored)
MSWD (of conc. & equiv.) = 1.02,
Probability (of conc. & equiv.) = 0.44

d Dolores Endoskarn

DO48SR-2
Concordia Age = 36.2±0.3 Ma
(95% confidence, decay-const. errs ignored)
MSWD (of conc. & equiv.) = 1.6,
Probability (of conc. & equiv.) = 0.016

e NW Cobriza Intrusion

CO23-30GC
Concordia Age = 35.7±0.3 Ma
(95% confidence, decay-const. errs ignored)
MSWD (of concordance) = 1.4,
Probability (of concordance) = 0.036

f Cobriza Endoskarn

CO7801-20ENS
Concordia Age = 35.3±0.3 Ma
(2σ, decay-const. errs ignored)
MSWD (of conc. & equiv.) = 1.06,
Probability (of conc. & equiv.) = 0.38

	Mem-brillo	Santa Teresa	Dolores E 1	Dolores E 2	Dolores E 3	Dolores W 1	Dolores W 2	Dolores W 3	Dolores W 4	Cobriza NW 1	Cobriza NW 2	Cobriza NW 3	Cobriza SE 1	Cobriza SE 2	Cobriza SE 3
	MGA	DQ-76 GD	DO-48 GM1	DO 48 GR1	DO 48 GR2	DJ-14 GM1	DJ-14 GR1	DJ-14 GR2	DJ-10 GM1	CO 2330 GR-W	CO 2330 GC	CO 2330 GR-E	CO 7820 GR-S	CO 7820 GR-N	CO 7816 GR
SiO_2	63.47	64.39	66.95	66.97	66.44	72.74	72.12	72.49	67.91	67.62	66.72	66.77	66.82	67.33	63.75
TiO_2	0.65	0.59	0.62	0.60	0.65	0.21	0.20	0.23	0.60	0.60	0.67	0.58	0.64	0.61	0.81
Al_2O_3	14.99	13.68	15.18	15.41	15.29	13.39	13.80	13.86	14.32	15.11	15.20	14.63	15.23	15.30	16.19
Fe_2O_3	3.89	2.80	3.54	3.40	3.36	1.42	0.97	1.33	3.22	2.70	2.48	2.82	3.86	3.65	3.50
MnO	0.06	0.05	0.03	0.03	0.03	0.03	0.02	0.04	0.03	0.03	0.03	0.04	0.04	0.04	0.03
MgO	1.21	0.77	1.11	1.05	1.13	0.32	0.31	0.36	1.02	0.83	0.97	0.81	0.88	0.82	1.20
CaO	3.77	5.30	3.44	3.32	4.07	1.73	2.79	1.91	3.63	3.91	4.44	3.98	3.25	3.35	4.98
Na_2O	2.26	1.55	2.93	2.82	2.97	2.75	2.09	3.20	2.52	3.31	3.22	2.86	3.28	3.34	3.75
K_2O	4.17	6.25	3.92	4.21	4.24	4.90	4.98	4.62	4.21	4.05	4.44	5.17	3.69	3.52	3.60
P_2O5	0.22	0.20	0.21	0.21	0.22	0.13	0.13	0.13	0.20	0.25	0.29	0.24	0.27	0.25	0.33
H_2O	2.18	1.20	1.22	1.17	0.84	1.20	1.13	0.90	1.03	0.84	0.74	0.95	1.18	1.08	0.99
CO_2	2.22	2.35	0.28	0.32	0.17	0.77	0.74	0.42	0.57	0.30	0.33	0.67	0.37	0.32	0.23
Li	79.54	61.85	41.31	97.96	78.15	47.61	27.87	33.38	44.12	67.62	58.32	54.50	71.98	65.39	53.69
Sc	13.08	74.60	11.58	20.29	24.60	4.02	5.29	6.05	10.65	6.45	10.55	8.24	6.06	5.06	11.39
Ti	5226.69	16942.39	5749.50	9846.83	11504.54	1514.72	1602.47	1645.11	5874.61	5079.77	7290.49	6958.94	5198.78	3708.66	6406.25
V	75.51	209.35	66.73	144.56	189.90	26.87	35.40	22.63	61.38	67.52	114.46	66.30	41.42	34.12	86.29
Co	9.75	15.33	7.22	11.96	13.90	1.78	1.23	1.68	7.32	5.03	6.51	6.70	6.11	4.45	7.46
Ni	5.33	5.90	4.32	7.90	10.26	1.50	2.16	1.51	4.46	4.49	6.01	6.57	3.45	2.55	5.60
Cu	23.78	520.44	66.59	61.72	96.39	74.49	127.46	53.76	300.30	16.85	49.94	91.44	33.61	6.51	60.55
Zn	82.93	n.b.	63.22	105.92	126.64	34.21	53.36	270.19	191.93	80.27	82.42	92.62	85.97	69.64	64.93
Y	44.09	49.96	40.71	77.23	87.56	36.66	44.30	40.35	39.05	36.61	50.97	40.58	33.16	23.78	36.98
Zr	189.79	197.27	122.29	295.58	276.17	118.22	123.92	139.90	166.20	169.80	215.04	160.09	170.69	92.61	137.93
Nb	28.82	63.02	30.70	60.21	65.73	37.89	45.53	47.43	27.17	30.64	49.48	43.73	34.91	23.44	28.50
Mo	8.62	113.02	17.14	11.28	29.08	70.72	25.87	9.93	61.69	10.29	22.60	57.70	2.34	1.75	4.17
Cd	0.90	5.61	0.40	0.63	0.66	0.78	2.23	11.48	5.80	0.88	1.00	1.23	0.18	0.15	0.48
Sn	17.32	227.49	21.64	47.46	39.64	15.06	22.67	26.62	31.15	8.42	17.64	50.24	5.52	5.03	15.09
Sb	4.38	30.71	1.06	3.36	3.01	2.40	4.43	3.70	2.24	0.75	0.94	1.32	0.23	0.15	0.27
Rb	412.71	458.02	362.50	793.67	668.57	386.18	483.21	507.74	332.63	381.96	510.89	549.01	297.17	219.72	334.66
Sr	953.32	2531.85	823.11	1606.51	1746.54	325.15	561.21	409.68	856.42	1147.06	1468.71	1224.31	1091.07	779.56	1360.42
Cs	30.25	33.87	26.65	72.11	28.77	19.74	31.14	46.97	14.49	19.16	19.22	24.53	15.09	11.67	16.36
Ba	2171.81	1745.72	1772.40	3690.36	3410.91	717.31	972.59	932.25	1645.02	1917.29	1930.95	2532.47	2061.30	1370.49	2211.27
La	88.25	85.74	78.83	154.09	118.99	32.68	33.53	33.37	84.54	82.41	108.71	107.21	114.88	63.57	127.71
Ce	174.15	176.05	157.95	311.17	245.65	69.59	71.45	70.99	167.91	173.30	227.17	219.45	224.81	126.09	253.71
Pr	23.32	24.41	20.91	41.20	33.51	9.25	9.70	9.67	22.30	24.42	32.55	30.24	30.33	17.23	34.70
Nd	89.43	94.91	81.72	160.47	134.86	35.50	37.86	37.37	85.84	99.11	132.93	120.80	116.79	68.12	135.85
Sm	17.22	17.98	16.29	32.42	29.58	8.57	9.61	9.02	16.39	20.46	27.75	24.26	21.47	13.64	25.45
Eu	3.80	3.68	3.70	7.16	7.24	1.21	1.06	1.23	3.73	4.33	5.74	5.05	4.44	3.25	5.62
Gd	14.12	11.91	13.53	26.84	27.67	7.77	8.57	8.34	13.08	15.84	24.52	19.40	16.71	10.23	19.25
Tb	1.88	1.74	1.83	3.39	3.42	1.30	1.50	1.41	1.70	1.96	2.67	2.21	1.90	1.28	2.22
Dy	9.97	10.85	9.41	17.75	18.78	7.52	8.72	8.04	8.93	9.24	12.70	10.50	8.60	6.15	10.09
Ho	1.76	1.97	1.62	3.01	3.23	1.34	1.54	1.43	1.52	1.41	1.85	1.56	1.28	0.93	1.51
Er	4.70	5.21	4.30	7.71	8.56	3.59	4.03	3.83	3.93	3.47	4.45	3.76	3.17	2.27	3.71
Tm	0.59	0.66	0.54	0.92	1.08	0.49	0.57	0.52	0.48	0.36	0.48	0.39	0.32	0.25	0.35
Yb	3.77	4.38	3.36	5.93	7.11	3.29	3.75	3.59	3.06	2.21	2.82	2.35	1.86	1.46	1.99
Lu	0.54	0.61	0.47	0.81	0.99	0.46	0.51	0.49	0.43	0.29	0.38	0.31	0.26	0.19	0.26
Hf	9.32	7.84	6.36	15.88	13.55	7.83	8.87	9.07	8.20	8.46	10.44	8.59	8.89	5.01	6.63
Ta	3.78	8.96	4.35	7.44	8.22	4.06	7.35	18.46	2.47	1.65	5.87	6.03	4.41	3.24	0.46
W	11.05	40.89	4.22	44.41	36.14	9.63	174.94	33.92	18.42	4.86	8.10	16.35	2.06	2.57	2.72
Tl	7.00	14.98	2.43	5.58	3.42	2.77	3.53	3.86	2.28	2.26	2.57	3.37	1.86	1.37	2.18
Pb	68.39	459.56	28.32	72.26	57.89	74.09	62.67	68.15	72.49	55.47	45.82	52.67	41.13	31.90	39.38
Bi	1.50	31.10	5.00	0.96	4.77	5.45	19.31	2.41	3.23	0.25	0.94	18.18	0.71	0.18	0.19
Th	34.46	28.86	33.09	75.70	55.25	18.68	21.28	20.36	32.62	40.58	41.49	41.45	45.21	24.09	38.72
U	11.40	32.96	12.17	25.74	30.50	39.39	50.77	40.55	11.33	16.28	15.91	15.82	20.59	9.98	10.18

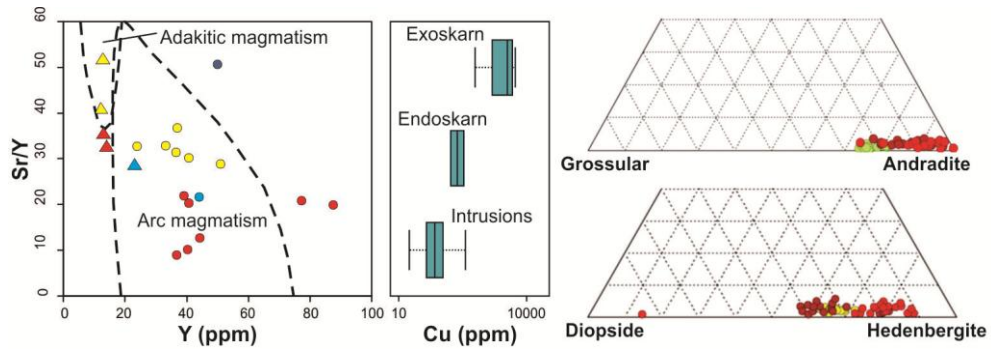| La_N/Yb_N	15.78	13.20	15.82	17.52	11.28	6.70	6.03	6.27	18.63	25.14	25.99	30.76	41.64	29.36	43.27
Eu_N/Eu_N^*	0.75	0.77	0.76	0.74	0.77	0.45	0.36	0.43	0.78	0.74	0.67	0.71	0.72	0.84	0.78

	Santa Teresa Exoskarn	Dolores E Endoskarn	Dolores E Endoskarn	Dolores W Exoskarn	Dolores W Exoskarn	Dolores W Endoskarn	Cobriza NW Exoskarn	Cobriza NW Exoskarn	Cobriza NW Exoskarn	Cobriza SE Endoskarn	Cobriza SE Exoskarn	Cobriza SE Endoskarn
	DQ-51 SK	DO-48 SR1	DO-48 SR2	DJ-14 SR2	DJ-10 SR2	DJ-10 SR1	CO 2330 SL	CO 2330 SG-W	CO 2330 SG-E	CO 7820 ES	CO 7820 SG-E	CO 7816 SG
SiO_2	42.10	46.18	58.09	67.59	55.54	48.41	36.82	37.42	41.60	55.51	40.56	36.10
TiO_2	0.12	0.05	0.69	0.16	0.73	0.03	0.16	0.19	0.15	0.69	0.06	0.03
Al_2O_3	3.23	4.82	17.61	11.42	14.67	0.60	2.85	4.19	3.79	18.70	3.97	1.61
Fe_2O_3	14.34	16.78	3.16	4.89	8.60	24.35	29.16	24.80	15.30	3.54	22.71	28.49
MnO	0.15	0.52	0.06	0.05	0.12	0.30	0.44	0.13	0.12	0.12	0.22	0.08
MgO	0.80	3.81	1.15	0.38	1.29	0.59	0.71	0.35	0.63	0.96	1.62	0.43
CaO	34.71	25.38	6.87	7.20	11.33	23.46	15.80	31.14	36.19	10.13	27.16	32.03
Na_2O	<0.01	<0.01	2.07	0.44	1.34	<0.01	<0.01	<0.01	<0.01	2.41	<0.01	<0.01
K_2O	0.04	0.30	7.63	4.10	2.95	0.01	1.40	0.19	0.01	5.54	1.10	0.02
P_2O5	0.10	0.36	0.24	0.13	0.25	0.16	0.15	0.23	0.12	0.29	0.03	0.08
H_2O	0.82	0.66	1.01	1.62	1.60	0.43	1.78	0.67	0.45	1.18	0.69	0.49
CO_2	2.78	1.00	0.96	0.99	0.98	0.86	3.09	0.38	0.95	0.28	1.18	0.72
Li	6.40	38.36	18.09	36.17	39.70	9.65	28.64	6.90	3.78	95.31	11.88	5.50
Sc	4.90	3.80	14.77	5.84	12.76	1.91	5.61	7.43	6.74	7.59	1.17	1.46
Ti	963.19	842.79	5833.77	1269.47	5998.58	259.95	1250.61	1456.85	1510.68	5533.29	381.37	223.75
V	293.98	656.72	75.68	51.92	70.41	126.02	217.85	285.38	715.09	51.51	91.98	42.11
Co	6.94	42.40	5.52	5.88	16.17	16.70	51.78	7.81	5.07	10.21	13.96	3.40
Ni	50.21	79.78	8.72	11.14	12.16	21.11	95.61	29.67	55.13	9.62	23.28	22.30
Cu	489.96	142.53	270.74	3816.85	873.45	201.85	34528.83	2640.09	1617.99	35.59	2997.72	1806.54
Zn	110.69	339.95	68.52	2849.44	371.03	81.03	1234.57	136.19	51.36	181.35	136.34	26.47
Y	19.60	63.31	50.39	28.42	39.66	16.22	18.72	32.04	50.39	45.98	15.18	11.84
Zr	66.60	63.43	143.81	92.10	213.00	22.07	91.40	109.36	156.08	157.89	26.82	26.44
Nb	5.00	6.53	36.51	8.15	29.96	3.09	5.00	5.14	9.50	43.04	3.83	1.92
Mo	6.49	8.41	47.29	62.86	55.16	227.13	10.89	3.61	11.18	24.57	2.29	5.57
Cd	6.75	2.17	1.05	149.77	13.70	1.18	47.59	20.63	20.85	0.94	18.47	28.31
Sn	1018.56	696.88	126.87	502.08	153.78	322.59	1367.33	1504.62	1442.69	37.09	1515.35	2753.16
Sb	22.82	9.02	2.78	966.77	16.22	0.83	9.70	0.73	6.89	0.46	0.66	0.81
Rb	2.96	52.43	497.09	294.19	214.07	1.22	79.09	11.93	2.65	405.39	55.14	3.05
Sr	59.25	102.84	1077.99	238.91	698.32	17.12	50.23	10.00	29.08	1654.74	25.75	4.63
Cs	1.27	9.00	21.07	23.45	19.12	1.31	32.52	10.48	2.67	43.66	8.90	5.18
Ba	13.42	137.50	2085.33	606.53	936.95	0.89	76.32	12.62	5.01	3604.44	88.83	2.16
La	9.79	20.31	102.89	20.95	66.97	5.74	3.90	3.91	13.33	87.10	42.45	12.97
Ce	22.06	39.58	193.79	40.35	138.00	19.80	6.71	13.94	30.55	206.97	63.81	54.31
Pr	3.32	6.11	25.76	5.11	18.57	3.23	0.96	2.47	4.72	30.68	7.26	7.43
Nd	13.91	29.47	98.51	19.13	72.57	13.66	4.19	10.47	21.05	126.98	24.88	21.48
Sm	2.46	8.28	18.81	4.45	14.31	2.51	0.99	2.17	4.74	26.58	3.93	2.06
Eu	1.12	1.84	3.30	0.38	2.74	0.80	0.31	0.91	1.35	3.71	1.33	1.85
Gd	2.36	9.67	15.12	3.96	12.64	2.35	1.17	2.34	5.00	21.98	3.02	1.84
Tb	0.33	1.46	2.02	0.68	1.63	0.29	0.18	0.36	0.74	2.53	0.33	0.18
Dy	1.98	8.73	10.73	3.90	8.41	1.69	1.10	2.27	4.48	12.16	1.66	0.90
Ho	0.41	1.78	1.88	0.71	1.44	0.33	0.23	0.46	0.93	1.82	0.29	0.17
Er	1.19	5.05	4.99	1.88	3.76	0.95	0.66	1.32	2.61	4.44	0.83	0.52
Tm	0.16	0.74	0.62	0.27	0.45	0.12	0.09	0.18	0.34	0.48	0.10	0.05
Yb	1.06	5.89	3.87	1.81	2.80	0.75	0.65	1.17	2.23	2.94	0.66	0.36
Lu	0.16	1.10	0.52	0.25	0.39	0.11	0.10	0.17	0.32	0.40	0.10	0.06
Hf	2.66	2.22	7.93	6.66	10.16	0.67	4.11	4.69	4.75	9.25	1.01	0.89
Ta	0.44	0.13	4.71	0.74	2.98	0.22	0.58	0.45	0.87	5.57	0.37	0.13
W	84.52	28.08	44.96	431.49	47.12	158.46	16.64	116.22	7.06	9.57	524.94	1210.29
Tl	0.11	0.81	3.17	3.40	1.86	0.05	4.28	0.99	0.13	2.53	1.05	0.24
Pb	109.76	46.22	17.11	6386.55	248.23	7.91	5.89	20.66	27.35	40.64	14.43	18.26
Bi	146.95	420.53	21.08	641.67	24.81	10.75	283.58	170.77	386.85	3.00	145.87	223.88
Th	3.62	5.70	40.57	15.74	28.88	1.77	5.95	4.04	8.68	43.43	2.65	4.34
U	17.78	7.60	9.50	48.52	12.59	20.56	14.21	11.62	27.27	18.55	12.65	43.15
La_N/Yb_N	6.23	2.32	17.92	7.80	16.13	5.16	4.05	2.25	4.03	19.97	43.36	24.29
Eu_N/Eu_N^*	1.42	0.63	0.60	0.28	0.62	1.01	0.88	1.23	0.85	0.47	1.18	2.91

Sample	Spike	K₂O [wt.-%]	⁴⁰Ar* [nl/g]	⁴⁰Ar* [%]	Age [Ma]	2σ [Ma]	2σ [%]
Santa Teresa	4950	7.88	9.00	96.79	**35.05**	**0.89**	2.5
Dolores E	4948	9.13	9.18	78.13	**30.92**	**0.41**	1.3
Dolores E	4949	9.18	10.59	86.23	**35.43**	**0.45**	1.3
Dolores W	4947	8.98	10.25	87.60	**35.07**	**0.55**	1.6
Cobriza SE	4943	8.98	7.92	97.46	**27.13**	**0.41**	1.5
Cobriza SE	4941	9.33	10.26	94.55	**33.80**	**0.36**	1.1
Cobriza NW	4934	8.88	9.9	95.41	**34.23**	**0.60**	1.8
Cobriza NW	4935	8.86	9.83	97.02	**34.06**	**0.59**	1.7

Sample	Re [ppm]	2σ [ppm]	^{187}Os [ppb]	2σ [ppb]	**Age [Ma]**
Standard 1 (ARM 2007)	11.3	0.1	3.3	0.03	**27.64**
Standard 2 (ARM 2007)	11.0	0.1	3.2	0.03	**27.70**
CO-MoS$_2$ 1	39.6	0.4	15.7	0.15	**37.80**
CO-MoS$_2$ 2	39.0	0.4	15.7	0.15	**38.34**
Calculated age					**38.07 ± 0.27**

- Geochemical and geochronological data of the Santa María de la Paz Cu-Au skarns
- Eocene intrusions emplaced in post-Laramide continental arc setting
- U-Pb and Re-Os data indicate contemporaneous magmatism and skarn mineralization
- Dominant andradite and hedenbergite compositions of skarn rocks
- Cu-Au together with Fe, Ni, Sn, Sb, Zn, W and Bi concentrated in exoskarn rocks