Hydrothermal activity along a strike-slip fault zone and host units in the São Francisco Craton, Brazil – Implications for fluid flow in sedimentary basins

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Abstract

This study combines multiscale analyses of geological, fault, fracture, and stable isotope data to investigate strike-slip deformation and channeling of hydrothermal fluids along the Cafarnaum fault and calcite veins at different distances from the fault, which is a structure in the São Francisco Craton, northeastern Brazil. Meteoric fluids with δD values near -45‰ and $\delta^{18}O$ values near -6.5‰ and temperatures at 40-70°C precipitated as calcite veins in the host carbonate units. The Cafarnaum fault, a N-S-striking vertical, ~170 km long fault zone, juxtaposes Neoproterozoic carbonate rocks in the western block and Mesoproterozoic siliciclastic rocks in the eastern block. A zone of restraining bends occurs at the central part of the fault, whereas termination zones of horsetail geometry occur at both ends of the Cafarnaum fault. These zones are marked by NW-SE-striking extensional faults that are oblique to the main N-S-striking fault zone, where hydrothermal deposits occur. The zone of influence of the Cafarnaum fault is ~20 km wide around the main fault. The fault formed during the Brasiliano orogeny (740-560 Ma) after Neoproterozoic carbonate platform deposition. In contrast with the host units, fluids along the fault zone originated in deeper levels of the crust and show much lower $\delta^{18}O$ values, indicating higher crystallization temperatures. These fluids caused brecciation in the Neoproterozoic carbonate host rocks, whereas a subsequent decrease in fluid pressure and cooling near the surface resulted in the precipitation of a hydrothermal paragenesis in veins, also affecting the host rock.

Keywords: carbonate veins, hydrothermal fluid, strike-slip fault, Salitre Formation, São Francisco Craton

1. Introduction

Sedimentary basins display different fluid migration regimes depending on the host rock, particularly in areas subjected to extensional tectonics. Sedimentary stratified layers may allow basinal fluids to migrate laterally parallel to bedding for hundreds of kilometers (Qing and Mountjoy, 1992). In most instances, sedimentary basins display limited vertical fluid flow due to impermeable layers; hence, fluid conduits cannot connect deep and shallow parts of a basin. Pore water usually has a low-velocity flow regime, and its primary geochemical values are therefore easily altered by reactions with host rock minerals and mixing with other fluids (Bjorlykke and Egeberg, 1993).

Vertical fluid flow pathways in sedimentary basins are associated with fault zones (Haneberg et al., 1999; Hardebeck and Hauksson, 1999). Depending on the structures and/or permeability properties, fault zones can either act as hydraulic barriers or as preferential conduits for geofluid migration (Gudmundsson, 2001; Rawling et al., 2001; Smeraglia et al., 2021; La Bruna et al., 2021). These characteristics are also linked to the several structural/diagenetic phases affecting the carbonate rocks from the earliest diagenetic stages (e.g., La Bruna et al., 2020). In fact, selective cementation and structural diagenetic processes are key factors in fault permeability control (Hausegger et al., 2010; Ngwenya et al., 2000).

Strike-slip faults create complex and heterogeneous permeability anisotropy and strongly influence fluid migration in crustal fault zones (Caine et al., 2010; Bense et al., 2013; Arancibia et al., 2014). A wide variety of processes at various scales can occur during fault growth and lead to a large range of fault architectures and properties that influence fluid flow behavior (Wibberley and

Shipton, 2010). The activity of major and weak strike-slip fault systems is influenced by fluid flow (e.g., Byerlee, 1990; Rice, 1992; Sleep and Blanpied, 1992; Evans and Chester, 1995; Zhang et al., 2001). The internal structure of strike-slip faults is dominated by vein arrays and hydraulic breccias. These features result from intense, deep-seated, and localized hydrothermal fluid flow (Cox and Munroe, 2016). Fluid flow history can be investigated in exhumed faults and fractures, which provide information about deformation mechanisms, fluid-rock interactions, and bulk chemical redistributions (Arancibia et al., 2014; Steyrer and Sturm, 2002). Among other features, synthetic faults, antithetic faults, deformation bands, joints, stylolites, veins, and breccia have been recognized in strike-slip fault zones affected by hydrothermal fluids (e.g., Fossen and Rotevatn, 2016; Choi et al., 2016; Liao et al., 2017; Peacock et al., 2017a, 2017b; Alsop et al., 2020; Ostermeijer et al., 2020). However, there is a debate about which of these structures, if any, exerts a primary influence on fluid flow and the role and origin of fluids in strike-slip fault zones (e.g., Gudmundsson et al., 2002; Gudmundsson, 2007).

Several studies show that hydrothermal deposits occur in the São Francisco Craton region, including those around fault zones, while the region remained tectonically stable during the Brasiliano/Panafrican orogenic cycle at 740-540 Ma (e.g., Almeida et al., 2000; Brito Neves et al., 2014). This study focuses on the Cafarnaum fault zone, which occurs as a lateral ramp (Fig. 1A, B, C, D). However, the relationship between the location and timing of hydrothermal deposit formation and fault geometry and evolution remains elusive.

This study is a multiscale and multidisciplinary approach that uses remote sensing, aeromagnetic data, field observations, petrography, and stable isotope geochemistry to compare the structural evolution of the hydrothermal system in the siliciclastic and carbonate host rocks along the Cafarnaum fault zone and the inner basin. We present stable isotope analyses on carbonate host rocks, veins, pockets, and fluid inclusions of the inner basin to reconstruct fluid-rock interactions and build a model to predict the development of hydrothermal activity on a regional scale, which can be used as a proxy for other basins elsewhere. New stable isotope data of fluid inclusions and veins and previously published data of sulfur in sulfides show that carbonate veins associated with fractures at the edge of the basin record much higher temperatures than those crystallized in the central part of the basin. This study also describes and discusses the kinematics, morphology, and magnetic characteristics of the fault zone and the formation of various types of hydrothermal dilation breccias in the damage zone. Finally, a comparison of the Precambrian Cafarnaum fault system and its host rocks with other faults that affect other carbonate and siliciclastic units helps understand regional predictability. This study concludes that fluid flow occurs mainly along extensional subsidiary faults and investigates the way they deform the host rocks. The isotope data indicate that fluids are meteoric in origin and, compared to the sedimentary basins, fluids that percolated the crystalline terrain may have circulated into much deeper zones.

2. Geological setting

The study area is mainly composed of Mesoproterozoic rocks of the Chapada Diamantina Group and Neoproterozoic units of the Una Group, primarily the Salitre Formation (Fig. 1D, E). The groups contain distinct formations and contrasting structural styles. Both major terrains are bounded by a strike-slip fault that we name the Cafarnaum fault in this study. It acted as a tectonic boundary between the aforementioned Mesoproterozoic and Neoproterozoic units (La Bruna et al., 2021).

The Chapada Diamantina Group is 1,000 m thick and includes the Morro do Chapéu Formation, which was deposited at ~1400-900 Ma (Pedreira et al., 1975; D'Angelo et al., 2020). This unit was affected by a first contractional inversion event that is mainly marked by symmetrical, N-S-trending, open folds (Danderfer et al., 2015; D'Angelo et al., 2020). High-angle fractures strike mostly N-S, NE-SW and NW-SE, and have a high degree of symmetry with the N-S regional folds (Danderfer et al., 2015).

The Salitre Formation is ~750 m thick in the central part of the Irecê Basin (D'Angelo et al., 2020), which was deposited in a carbonate pelitic marine basin (Misi et al. 2005, 2011) at ~750 Ma (D'Angelo et al., 2020). This sequence was deposited in the Irecê Basin, an asymmetric graben with an approximately N-S-oriented axis that plunges toward the north (Lagoeiro, 1990; Kuchenbecker et al., 2011; Brito Neves et al., 2012; D'Angelo et al., 2020). The Irecê Basin was inverted in the Brasiliano orogeny, with a peak at ~600 Ma, which resulted in anomalous deformation concerning adjacent domains, with a series of south-verging fold and thrust systems (Lagoeiro, 1990; Teixeira et al., 2019; D'Angelo et al., 2020).

The carbonate units of the Irecê Basin have similar Pb-Pb isochron ages and paleomagnetic poles, which fall close to ~520 Ma. This age is consistent with the Gondwana supercontinent's apparent polar wander path and indicates that isotopic and magnetic systems reset those of the Cambrian (Trindade et al., 2004). This event was related to regional-scale fluid migration and subsequent mineralization at the end of the Brasiliano orogenic cycle (Trindade et al., 2004).

An E-W-oriented magnetic telluric section across the Irecê and Morro do Chapéu Basins reveals lithospheric resistive blocks bounded by major conductive deep zones, which are interpreted as faults. It shows that a lithospheric conductor, interpreted as a suture zone, occurs between the Neoproterozoic Irecê Basin and the Chapada Diamantina Group (Fig. 1D). The high conductance zone is a combination of high porosity and high fluid salinity (Padilha et al., 2019).

Detailed geological mapping on both sides of the fault indicates a great number of occurrences of hydrothermal minerals associated with faults. These occurrences encompass metals such as Au, Pb-Zn, and Ba. These metals occur in sulfides associated with quartz veins in dolomite units close to the main faults. In a few cases, minerals such as barite also occur in the host carbonate rocks (Sampaio et al., 2001).

More detailed studies have also investigated hydrothermal silicification and dolomitization in a few karst systems. Several works, conducted in the São Francisco Craton, have already investigated cave geometry, stratigraphy, geochemistry, and mineralogy to indicate that fault and fracture systems were used as conduits for deep-seated fluid flow (Klimchouk et al., 2016; Cazarin et al., 2019; La Bruna et al., 2021; Pontes et al., 2021). In another case, approximately 100 km to the south of the study area, a N-S-striking, strike-slip fault in the southern part of the Irecê Basin was the pathway for fluid flow confined to the Salitre Formation during the Brasiliano orogeny. The first stage of Mg-rich fluids caused extensive dolomitization in the Salitre Formation, which was subsequently followed by Si-rich fluids that caused pervasive silicification in the host units (Bertotti et al., 2020).

3. Methods

The present study integrates (1) remote sensing and structural investigation, (2) Geophysical data and processing, (3) sampling, (4) mineralogy and petrography, (5) stable isotope analysis of veins and host rock, and (6) isotope geochemistry of fluid inclusions. We used the Shuttle Radar Topographic Mission (SRTM), ALOS-PALSAR to map regional structures, and unmanned aerial vehicle imagery for a detailed investigation of tectonic features (Fig. 2). The aeromagnetic data used to map fault segments are from the Centro Norte Bahia Project is an airborne magnetic survey carried out by Companhia Baiana de Pesquisa Mineral (CBPM) (Fig. 3). The petrography, mineralogy, isotope, and fluid inclusions are based on the analysis of six outcrops in carbonate units of the Salite Formation on both sides of the Cafarnaum fault. We present a complete description of data and methods in the supporting material section (Methods – supporting material).

4. Results

4.1 *Qualitative field fracture analysis*

Different fracture types were distinguished; joints display their peculiar plumose morphology (Pollard and Aydin, 1988), and are compart   mentalized or not within single beds (Fig. 4). For this reason, they are here named stratabound (SB) and non-stratabound (NSB) fractures. Veins are also SB and NSB, but in some outcrops they are subvertical and parallel to the tilted bed layers (Fig. 4C, D and F). Clustered fracture and vein networks were in the proximity of fault zones (Fig. 5B,C, D and E). In particular, the high-resolution qualitative structural analysis shows the following fracture sets: subvertical NW-SE fractures and veins (Fig. 4G, H and Fig.5B,C, D, E, F, G and H); minor subvertical NE-SW fractures and veins (Fig. 4G and Fig.5B,C, D, E, F, G and H); minor subvertical N-S fractures and veins (Fig.5C, D, and F); and subvertical E-W bed-parallel veins (Fig. 4C, D and F).

4.2 Macroscale geometry and kinematics of the Cafarnaum fault

The compiled structural map presents the primary structural alignments in an area of 38,000 km^2 (Figs. 2A, B, C, 3A, B). The tectonic structures were sorted into strike-slip faults, normal faults, reverse faults, and fold hinges based upon new original data interpretation and previous geological mapping (Cazarin et al., 2019; D'Angelo et al., 2019; Ennes-Silva et al., 2015; Souza et al., 2003). The satellite alignments were divided into the following three fault sets: NNE-SSW, NE-SW, and NW-SE. The NNE-SSW set is generally associated with strike-slip left-lateral faults, as already presented by D'Angelo et al. (2019) and Danderfer Filho et al. (2015). A zone of restraining bends coincides with an uplifted area (Fig. 2A). Additionally, drag folds occur on the west side of the Cafarnaum fault. The folded structures are E-W-striking thrusts of the Irecê Basin that bend where they reach the Cafarnaum fault. Bed layers associated to these thrust faults were tilted to the subvertical position (Fig. 4A). In some case, the aforementioned subvertical bed interfaces were affected by shearing as displayed by several kinematics indicators (Fig. 4B). Many mineralized portions documented as bed parallel veins occur along bed interlayers (Fig. 4C, D and F). Some of the thrust faults display drag folds as they approach the Cafarnaum fault. In contrast, the NE-SW- and E-W-oriented sets are composed of reverse faults, as shown by D'Angelo et al. (2019) and Reis et al. (2013).

The NW-SE fault set has been interpreted as composed of normal faults (D'Angelo et al., 2019). Termination zones of horsetail geometry occur at both ends of the Cafarnaum fault (Fig. 2C). A few minor faults associated with veins and breccia bodies also occur at the central part of the fault zone, as at the MAM site (Fig. 5). These zones are marked by NW-SE-striking extensional faults located at the extensional quadrant of the main N-S-striking fault zone (La Bruna et al., 2021). There, hydrothermal deposits concentrate on a 20 km wide zone on both sides of the central fault (Fig. 2A, C). Several hydrothermal minerals (e.g., barite, galena) were documented in the Mam outcrop (Fig. 5B, C, D and E). In these sites, complex vein/fracture networks were observed. Both veins and fractures form a principal NW-SE striking set and a minor NE-SW set.

Both the NE-SW- and NW-SE-striking fault sets terminate against the NNE-SSW- to N-S-striking fault set. Eastward from the Cafarnaum fault, a larger folded zone was documented (Fig. 2B, C). Previous works have described how this sector is affected by several anticlines and synclines (Cazarin et al., 2019; D'Angelo et al., 2019; Danderfer Filho et al., 2015; Ennes-Silva et al., 2015; Souza et al., 2003). The fold hinges mainly trend along the NNE-SSW to N-S directions (Fig. 2B, C).

An area of ca. 14,000 km^2 was analyzed for structural magnetic lineament map characterization (Fig. 3A, B). The 2,818 documented lineaments were sorted into , I-order , II-order, and III order lineaments. The I-order lineaments are related to regional-scale magnetic features and are composed of a major NE-SW set and minor sets striking N-S and E-W, respectively. The II-order lineaments are characterized by a major NE-SW lineament and a minor NW-SE to WNW-ESE set associated with secondary magnetic anomalies. Both I- and II-order lineaments are crosscut by the III order lineaments.

The III order lineaments exhibit a singular magnetic pattern, distinguished by striking high-amplitude magnetic lineaments with the extension of dozens of kilometers (Figs. 3A, B). They occur isolated or comprising sets with main NW-SE and minor NE-SW orientations. Sometimes, they are stepwise segmented (en echelon) and shifted by hundreds of meters. They truncate other magnetic lineaments in high to moderate angles, indicating a more recent geological event. Due to high magnetization contrast with bedrocks, linear and extensive waveform, and sparse spatial distribution, we associate these magnetic lineaments with mafic dikes as many authors elsewhere (e.g., Schwarz et al., 1987; Demarco et al., 2020). In fact, the NNW-SSE trending Chapada Diamantina mafic dike swarm is intrusive into the Mesoproterozoic sedimentary sequences of the Espinhaço Supergroup within the Paramirim Aulacogen (Brito, 2008; Silveira et al., 2013). The magnetite-bearing dikes are fine to medium-grained diabases. Recently Pessano et al. (2021) associated NW-SE oriented magnetic anomalies in the central portion of the São Francisco Craton with Mesoproterozoic dikes of the Chapada Diamantina swarm.

4.3 - Hydrothermal vein and breccia characterization

Two main types of structures related to hydrothermal activity occur in the Cafarnaum fault zone and its surroundings. The first type is hydrothermal breccias, which mainly occur in dilational jogs. The second is calcite veins, which are widespread in the fault zone and the host rocks away from the fault. Two sites of hydrothermal breccias occur along NW-SE striking extensional faults, which we describe below. In addition, we describe four sites with calcite veins at varying distances from the Cafarnaum fault.

Hydrothermal breccias are characterized by the interaction between rocks and hydrothermal solutions and are geometrically characterized by several parameters, such as morphology, particle size distribution, fabric, and expansion radius (Jébrak, 1997). Chemical and physical mechanisms can form these breccia bodies: the first by selective dissolution and the second by the excess tension exerted, which exceeds the tensile resistance of the material, or in some combination. The analyzed bodies are classified as mosaic breccias that are formed by fluid-assisted breach (hydraulic fracturing) using the classification given by Jebrák (1984b). Carbonate clasts are present, and clasts that are larger than 2 mm range between 60-75% of clasts and 75-100% of clasts.

Hydraulic breccias are rocks composed of angular to subangular fragments of dimensions ranging from 0.4 cm to 5 cm that are cut by several generations of fractures and veins. The fragments are present throughout the breccia bodies and are derived from adjacent rocks. Generally, they are monolithologic and represented by carbonate rocks corresponding to the Salitre Formation.

Carbonates also contain calcite and quartz geodes surrounded by intense oxidation (limonitization). The interfragmentary filling is composed of iron oxide or quartz and calcite cement. The oxidized matrix is probably formed to replace rich materials in iron from the cementing fluid. Quartz is associated with calcite, galena, and malachite. There is intense veining by a network of veins with a branched structure that range from millimeters to centimeters thick and reach 30% of the total volume, and calcite veins of lesser thickness are related to quartz veins.

The description of carbonates can be compared to descriptions made by Souza et al. (1993), such as the association of intensely closed algal laminites corresponding to the Nova América inferior subunit (transgressive cycle III) at the MEL site, as well as area descriptions by Misi (1975) of fine dolomites with ankerite, barite and galena and light dolomites with millimeter bands, calcite impregnations and microcrystals of pyrite and galena. Nevertheless, occurrences only include sedimentary gaps along the Irecê Basin (Bonfim et al., 1985, and Souza et al., 1993).

The descriptions were made under transmitted light optical microscopy of the samples corresponding to MAM and MEL sites (Fig. 2A, C); the samples were divided into laminated carbonates with veins, laminated carbonates with a brittle aspect, and only the veins. The composition in these three divisions presents the same mineralogy in carbonates and the same mineralogy in the veins, differentiated by laminar and massive textural aspects in the case of carbonate alteration and fragmented textural aspects.

4.4 Mineralogy, texture, and isotope geochemistry

Sites from the central part of the basin (SOR, IRE, and ACH) and the eastern block (FAR) (Fig. 2C) are large carbonate pavements in which primary sedimentary features are observed. Except for the FAR site, these carbonates display vertical bedding and are crosscut by centimetric calcitic veins.

The limestones from the SOR site consist of microbial mats. The beds are oriented subvertically within tight N-S-trending folds (Fig. 2C). Two types of veins are observed at the SOR site. The first type of veins formed on transverse fault planes, which originate in E-W-striking low-angle thrust faults, predating folding to the present-day subvertical position (T16 and T19). The second type forms N-S-trending veins. These veins are associated with younger N-S shortening (T24). Isotope profiles across the veins reveal no significant difference in $\delta^{13}C$ and $\delta^{18}O$ concentration between the carbonate host rock and the transverse fault carbonate filling (Fig. 6A-D).

The FAR site (Fig. 6E-H) consists of stromatolite bioherm colonies. Two veins were analyzed. The first vein (T9) occurs in inter-stromatolite silt crosscut by a sharp-edged 2.2 mm thick vein, filled with mosaic equidimensional transparent calcite varying from 0.05 mm to 0.2 mm. The other vein (T10) crosscuts a stromatolite unit. It has two different calcite fabrics: an equidimensional mosaic with oriented sparry calcite crystals varying in size from 0.1 to 1 mm and a milky white area with no calcite crystals. Most calcite veins from the FAR site display lower $\delta^{13}C$ and $\delta^{18}O$ values than the stromatolite host rock. Exceptions are a few carbonate samples from the vein that crosscut the inter-stromatolite silt (Fig. 6G-H).

The ACH site consists of subvertical NNW-dipping dolostones. The present-day NNE-SSW burial fault carries most veins and is more prominent than its conjugate NW-SE counterpart (Fig. 7A-D). Veins at the ACH site lack signs of shear and are syntaxially filled with blocky crystals. In addition to veins, the ACH site contains a pocket filled with crystal precipitates (T5) in which borders are vein wall remnants and dissolved host rock peloids (Fig. 7B-C). Since these pockets dissolve burial-related fractures and faults, they formed later than the burial fault set. In general, ACH samples show a higher porosity than other sites. Isotope data across these veins reveal much lower $\delta^{13}C$ and $\delta^{18}O$ values than the isotope values of the host rock (Fig. 7C-D).

Carbonate rocks of the IRE site consist of thinly layered (0.2-20 cm) black limestones with local slumps. The beds are vertically tilted and folded, with an orientation of 355/86 (dip azimuth direction). Two types of veins are present (Fig. 97E-F): thinner (<1 cm) bedding-perpendicular and bedding-parallel pre- or synfolding veins and thick veins (20 cm) filled with a mixture of calcite and barite that irregularly crosscut folded bedding. They are syn- or post-folding veins. Similar to the SOR site veins, IRE veins have isotope values similar to the host rock (Fig. 7E-F).

In contrast to sites in the central part of the basin, sites at the basin edges (i.e., MEL and MAM) are strongly deformed and exhibit pervasive hydrothermal features and hydraulic hydrothermal breccias (Fig. 8A-C). Samples from the MEL site are mostly breccias with white calcite cement. Previous studies by Misi et al. (2005) argue that the Salitre Formation stratigraphy controls the Pb-Zn concentrations. According to these authors, the Pb-Zn ore is associated with silicified stromatolites that overlie a shallowing-upward sequence (Unit B1). The MEL site is located in a flat area where sites are restricted to trenches dug by mining operations. Samples may exhibit primary lamination similar to rocks of the Salitre Formation. These features are obliterated by tectonic and hydrothermal processes toward the center of the brecciated zone at the outcrop scale (Fig. 8A). Clasts of primary carbonate rocks may also occur in the hydrothermal breccia cemented by white calcite devoid of laminations (Fig. 8B). Secondary vugular-type porosity that is less than 1% in the area is also observed under the microscope. The limestones and breccias are crosscut by two generations of veins: one measuring 4 mm thick and made of calcite and, quartz microcrystals and a second measuring approximately 0.3 mm thick and made of quartz. The host carbonate and the cement display quite distinct mineralogy. The primary

Salitre carbonates consist mainly of calcite, dolomite, ankerite, siderite, iron oxide, and limonite. SEM, XRD, and QUEMSCAN data indicate that the veins and hydrothermal breccias display complex mineralogy, where the main minerals are calcite, dolomite, galena, barite, quartz, sphalerite, illite, chlorite, zincite, cerussite, malachite, magnesite, apatite, and chalcedony. Barite, apatite, chlorite, and quartz are concentrated along fracture zones (Fig. 8D-G) and, in some instances, may form larger aggregates. Thin section observations indicate that tectonic and hydrothermal processes were accompanied by the formation of stylolites, dolomitization, silicification, limonitization, microfractures, folding, and minerals with wavy extinction.

Samples (Figs.8D and E) at the MEL site display different facies of carbonate breccia and isotope $\delta^{13}C$ and $\delta^{18}O$ analyses performed at specific points in the samples. While the $\delta^{13}C$ values range between 0.22‰ and -2.24‰, the $\delta^{18}O$ values vary from -6.16‰ to -12.67‰. In most instances, the primary limestone fabric was replaced by milky carbonate with large anhedral crystals. Sample in Fig. 8C displays a cyclic succession of milky calcite and iron-rich dolomite crosscut by veins containing galena. High-resolution $\delta^{13}C$ and $\delta^{18}O$ data indicate that these samples may have an area with homogenous isotope values (Fig.8D-E), as well as areas with variable isotope values.

The MAM site is also located in a flat area in which sites are restricted to trenches of the mining operation. Centimetric veins of milky quartz occur in the carbonate host unit. As at the MEL site, XRD and SEM data at the MAM site indicate galena, zincite, ankerite, dolomite, cerussite, apatite, magnesite, anglesite, chlorite, and illite. However, in contrast to the MEL site, the MAM site exhibits strong silicification that may completely obliterate the primary carbonate texture. For instance, the QUEMSCAN images exhibit carbonate breccias replaced by silica in which ghost clasts can still be identified. Pores and laminated illite and chlorite areas indicate that silica-rich fluids replaced mostly carbonate minerals

4.5 - Fluid inclusions

Table 01 presents the H and O isotopic compositions of fluid inclusions for 10 samples from the ACH, IRE, and SOR sites in the Irecê Basin and at the FAR site in the eastern block of the Cafarnaum fault. The supplemented materials detail linearity and memory effect corrections applied to the H and O fluid isotope data. Table 01 also shows the average $\delta^{18}O$ isotopic composition of the carbonate associated with the fluid inclusions and the calculated temperature based on the isotope fractionation between calcite and water. The calculated temperature range is 40-74°C, with the highest values obtained in samples from the ACH and FAR sites

Except for one sample from the ACH site (ACH01.3Aa T5-1, left), all samples display negative δD_{SMOW} values. Fig. 9 plots the H and O isotope values with the global meteoric water line (GMWL) by Rozanski et al. (1993) and shows that the trending lines of samples from the ACH and FAR sites converge to a δD value of approximately -45‰ and a $\delta^{18}O$ value of -6.5‰.

5. Discussion

5.1 – Fault evolution and hydrothermal fluids

Cratons are composed of thick and cool lithospheric keels with high resistivities and low porosities (e.g., Ferguson et al., 2012; Selway, 2014). However, several studies have increasingly indicated that cratons present low-resistivity zones in the lithosphere that behave as weakness zones prone to deformation, such as ductile shear zones and faults (e.g., Pinto et al., 2010; Thiel and Heinson, 2013; Dong et al., 2015). These shear zones/faults provide a high permeability and are pathways for deep-seated fluids to ascend through the whole lithosphere (Caine et al., 2010; Bense et al., 2013). The study of hydrothermal fluids in fault zones in cratons may explain the permeability of fault zones and host units and deep geothermal exploration constraints (Taillefer et al., 2017). The boundary between the Irecê Basin and the Chapada Diamantina Group is marked by the Cafarnaum fault (Figs. 1, 2) (La Bruna et al., 2021), which coincides with a high conductor mapped by a magnetotelluric survey (Fig.10). This zone was prone to hydrothermal activity and is consistent with high porosity-permeability, high-fluid salinity, and sulfide emplacement. In a few cases, it served as a conduit for mafic volcanism (Teixeira et al., 2017; Padilha et al. 2019).

Faults behave as high permeability conduits that facilitate fluid flow in the Earth's crust (Cox and Munroe, 2016). Deep-seated hydrothermal fluids precipitate minerals that form veins and breccias and decrease the permeability of the lithospheric fault zones (Sibson et al., 1988, 1990). The precipitation of hydrothermal minerals in fault zones and host rocks is caused by decompression and cooler conditions (Calvin et al., 2015). Therefore, based on the characteristics presented here, the Cafarnaum fault was a structure prone to hydrothermal activity. It controlled the upward hot fluid flow, indicated by the relationship between fault geometry and hydrothermal deposits (Fig.10).

. Hydrothermal fluids channelized along faults can affect thousands of square kilometers, even in nonmagmatic settings (Nabavi et al., 2020). The hydrothermal activity in faults with shallow crustal levels under fluid overpressure is controlled by the geometry of the crustal-scale fault zone (Bellot, 2008). Dilational jogs flanking continental-scale strike-slip faults, for example, are locations prone to hydrothermal boiling and implosive brecciation (Sibson, 1987). Active examples of hydrothermal activity in dilational jogs occur in compressional settings such as New Zealand (Brathwaite et al., 1986 in 24) and the French Pyrenees (Taillefer et al., 2017).

We interpret the N-W-striking faults that arrest against the main N-S-trending Cafarnaum fault as dilational jogs that facilitate hydrothermal fluid ascension and flow (Fig.10). Hydrothermal minerals are concentrated in dilational jogs on both sides flanking the Cafarnaum fault, either on carbonate units in the western block or mainly on siliciclastic units in the eastern block (Fig. 2). This indicates that the structure, rather than the lithology, controls the fluid flow along the fault.

Hydrothermal breccias occur in dilational jogs on both sides of the main Cafarnaum fault (Fig. 2A, C). These breccias form when fluid migration becomes explosive (e.g., Jébrak, 1997). Subsequent precipitation of hydrothermal minerals forms breccias and heals the fault, decreasing their permeability (Katz et al., 2006; Taillefer et al., 2017). Fluid flow and subsequent precipitation have been interpreted with the seismic cycle and fault-valve behavior, influencing breccia occurrence (Taillefer et al., 2017).

The results shown in this study document how strike-slip faults such as the Cafarnaum fault are efficient pathways for fluids and that these fluids caused the widespread silicification and the precipitation of Ca-bearing minerals. A recently performed in the Morro Vermelho Karst System, located some 150km to the S of the Cafarnaum fault and developed within the same carbonate succession, provides more insights into the temporal succession of fluid circulation and precipitation/dissolution (Bertotti et al., 2020). During the first stage, fluids flowed along two main aquifers, the Chapada Diamantina quartz arenites and the overlying Salitre Formation carbonates, separated by the Bebedouro Formation glacial sediments aquitard. The flow was associated with pervasive dolomitization of a 100s of m wide body overlying a deep-seated strike-slip fault in the carbonates. With increasing displacement, the strike-slip fault grew upward (e.g., Dooley and Schreurs, 2012), thereby first affecting the Chapada Diamantina aquifer and eventually reaching the Salitre carbonates. With establishing a through-going fracture zone, Si-rich fluids previously confined to the Chapada Diamantina aquifer invaded the Salitre aquifer, causing widespread dissolution and karst formation and precipitation of Si both in the host rock as a silica-crust coating the caves. We suggest that such a temporal succession could also be applicable to the mineralizations of the Cafarnaum fault zone.

5.2 – Geochemistry of hydrothermal fluids, fluid pathways and tectonics

Fluid flow in the crust is a powerful mechanism to remobilize chemical elements and concentrate metals of economic interest (Heinrich and Candela, 2014, Yardley and Bodnar, 2014).. The efficiency of heat transfer and chemical remobilization depends on heat and chemical gradients, fluid-rock interactions, and tectonic settings. Many studies have addressed the question of how deep fluid penetrates the crust (e.g., Nesbitt and Muehlenbachs, 1989; Fricke, Wickham et al., 1992; Haines, Lynch et al., 2016). Most authors agree that fluid may penetrate as deep as 10 to 15 km into the crust, mainly in crystalline terrains submitted to an extensional tectonic regime.

The isotope data presented here show that fluid sources in the central part and at the Irecê Basin edges had the same origin but underwent distinct pathways. The new data presented in this study allow a discussion of the source of these fluids, their primary isotopic composition, their interaction with the sedimentary rocks on both sides of the Cafarnaum fault, and how deep they may have penetrated each kind of terrain.

Different generations of carbonate veins and breccias crosscut the sedimentary rocks of the Irecê Basin. Figs. 6 and 7 show that carbonate veins from the central part of the basin do not display significant carbon and oxygen isotope differences relative to the carbonate host rock. More significant isotopic differences occur in samples from the ACH and FAR sites, where the veins present more negative isotopic values than the host rock (Fig.6).

Data in this study suggest that the $\delta^{18}O$ value of the carbonate veins may be explained by a meteoric fluid source (Fig.11), by a higher temperature of crystallization (Table 02) of these carbonates, or by the combination of both processes. The oxygen isotope fractionation between calcite and water varies from 28‰ to 7‰ in the temperature range of 25-250°C (Chacko et al. 1991; Kim, O'Neil et al., 2007; Chacko and Deines, 2008). In contrast, the low $\delta^{13}C$ values observed in the carbonate may only be explained by an external source of carbon, since the carbon isotope fractionation values between calcite and HCO_3^- and calcite and CO_2 are much less than 4‰ at temperatures below 200°C (Deines et al., 1974; Chacko et al., 1991; Chacko and Deines 2008). Samples from the MEL site, which are located at the edge of the basin, display even more negative oxygen isotope values. As shown in Fig. 11, isotope data from this site display a narrow range of $\delta^{13}C$ values and a wide range of $\delta^{18}O$ values. Compared to the veins from the central part of the Irecê Basin, the lower $\delta^{18}O$ values of their carbonates indicate interactions with more ^{18}O-depleted fluids or higher crystallization temperatures.

Fig. 11compares the isotopic composition of the carbonates studied here with previous isotope data reported for the same area. The diagram shows that the data in this study have a wide range of $\delta^{18}O$ (-13.0‰ to 1.8‰) and $\delta^{13}C$ (-10‰ to 10‰) values. However, most of our samples have a narrower range of $\delta^{13}C$ (-5‰ to 1‰). The exceptions are samples from the IRE site that exhibit higher $\delta^{13}C$ values and a few samples from the ACH, FAR, and SOR sites that present $\delta^{13}C$ values below -5‰. Samples from the IRE site are associated with ^{13}C-enriched carbonates from the upper section of the Irecê Basin and plotted as squares in Fig. 9 . These primary high $\delta^{13}C$ carbonates have been reported in both the Irecê Basin (Misi 1988, Misi and Kyle 1994, Borges, Balsamo et al. 2016, Caird, Pufahl et al. 2017) and other Neoproterozoic basins (Santos, Alvarenga et al. 2000). Carbonate veins with $\delta^{13}C$ values below -5‰ are probably related to the same fluid that is responsible for the carbonates that formed the calcretes previously described in the basin (Borges, Balsamo et al. 2016, Caird, Pufahl et al. 2017). Published isotope data of these carbonates, plotted as "stars" in Fig.11, also present low $\delta^{13}C$ values.

The source of fluids related to the carbonate veins from the central part of the Irecê Basin may be further constrained by the isotopic composition of fluid inclusions trapped in the carbonate veins. Based on the oxygen isotopic composition of these fluid inclusions and the associated carbonate, we estimate the temperature of carbonate crystallization to be between 39 and 67°C (Table 02). These temperature estimates were based on Kim and O'Neil (1997) oxygen isotope fractionation equation between calcite and water. Since calcite and fluid-inclusions may be affected by post-entrapment isotope exchange during exhumation (Nooitgedacht et al., 2021), these results should indicate minimum temperature conditions. Assuming an average thermal gradient of 30 C/km, these fluids circulated at depths reaching 1000 m within the crust. Fig. 9 displays the mean global meteoric water line by Rozanski et al. (1993) and the hydrogen and oxygen isotope values of these fluid inclusions. It also shows trending lines for fluid inclusions from the ACH and FAR sites, indicating that they converge to a δD value near -45‰ and a $\delta^{18}O$ value near -6.5‰ along the mean meteoric water line (Fig. 9). We argue that these isotopic values represent the local meteoric water, which upon interaction with the host rock changed its isotopic composition along the mixing lines. A similar process has been described in active hydrothermal systems (Criss and Taylor Jr, 1986), in which there is also a more extensive range of $\delta^{18}O$ values compared to δD values.

The isotopic variation observed in Fig. 11 may be explained by different geological scenarios. Arrows I and II represent veins formed by mixing meteoric fluids and carbonate host rocks of the inner part of the basin at low-temperature conditions (between 30 and 40°C). Arrow I indicates mixing between these fluids and carbonates from the lower section. In contrast, arrow II represents the mixing between these fluids and the ^{13}C-enriched carbonates from the upper section. Arrow III represents carbonates formed by the same fluids as those of the calcretes, which have more negative $\delta^{13}C$ values. Samples from the MEL site, represented by arrow IV, fall within the same range of $\delta^{13}C$ values for most samples from the central part of the basin. However, they also have more negative $\delta^{18}O$ values, indicating that isotope exchange between the meteoric fluids and carbonates alone may not be reconciled with the observed data. We argue that carbonates from the MEL site crystallized from the same meteoric fluid but at higher temperatures. These fluids percolated through conduits that allowed them to reach deeper parts of the crust and return to shallow crustal levels without losing much heat. Compared to thrust systems alone, thrust followed by strike-slip and extensional faulting may provide deep fluid conduits. Based on hydrogen isotopes, Nesbitt and Muehlenbachs (1989) concluded that the tectonic regime might drastically control the depth of fluid interaction in the crust. This interpretation also agrees with previous studies based on fluid inclusions and sulfur isotope geothermometry performed in the MEL site area (Misi and Kyle 1994, Misi, Iyer et al. 1999, Misi, Iyer et al. 2005), Fluid-rock interactions may also explain the presence of base metals in these high-temperature veins, suggesting that these chemical elements were scavenged from deeper crustal levels.

The role of deep crustal fluids at the MEL and MAM sites is further suggested by the petrographic and mineralogical features observed at these sites (Fig. 8). In addition to the high concentration of base metals (e.g., Pb, Zn, Fe), these sites display a pervasive replacement of the primary carbonates by silica. Silicification events are recognized as a diagenetic process in which Si-rich fluids affect a host rock, modifying its texture and mineralogy (Menezes et al., 2019). For example, Haldar and Tisljer (2014) documented a silicification process where opal/chalcedony/low-temperature quartz replaces calcite/aragonite/dolomite. The percolation of meteoric fluids at the deep crustal level provided the required conditions to mobilize silica at the MEL and MAM sites.

Deep meteoric fluid circulation along the Carfarnaun fault is comparable to other worldwide geological examples in which surface waters penetrate along tectonict structures. For instance, based on the Friedman and O'Neil (1977) isotope fractionation diagram, Mozafari et al. (2015) reconstructed the composition of the parent fluids that were in equilibrium with the vein infill in the Jabal Qusaybah Anticline (Adam Foothills, North Oman). The authors discussed a paleofluid evolutionary model related to the deformation front of the foreland fold and thrust belt. The strike-slip tectonic regime introduces a different type of fluid flow linked to the fault zone. The shifts in the stable isotope values forming different fields with comparable values (Fig. 12) possibly originate from different phases of strike-slip movement. A similar spread in the fluid inclusion isotope ratios was discussed by de Graaf et al. (2020) after analyzing the wide variety of vein-type mineralization caused by deep-seated brines in the Hartz Mountains, Germany. Other studies examined the complex recrystallization processes along dolomitization fronts causing dissolution of the host limestones and precipitation of dolomite crystal structures depending on the porosity-permeability properties of the sediments present in the fault systems (Koeshidayatullah et al., 2020).

Similar to the Cafarnaun fault, the interplay between tectonics and fluid circulation has played a major role in the evolution of the inner Northern Apennines. As shown by Brogi et al. (2020), active transfer zones associated with an extensional tectonism control the deposition of travertine deposits by enhancing fluid circulation. Other studies in the same area have shown that these trending faults have also controlled the development of magmatic activities (Brogi et al., 2021) and Hg-Sb ore deposits (Brogi et al., 2011), further suggesting that these structures may connect different geological systems and play a major role in the remobilization of chemical constituents. They also indicate that competition between crustal stretching and surface uplift continuously switches the local intermediate stress axis, thus promoting quick changes in the direction of the maximum permeability (Liotta and Brogi, 2020). These changes further promote lateral and vertical migration of fluids within the system.

6. Conclusion

This study in the São Francisco Craton focuses on the hydrothermal activity in the Cafarnaum fault and its host rock and yields the following conclusions. The São Francisco Craton is a cold and thick block preserved from deformation in the Brasiliano orogeny (740-580 Ma). However, a few tectono-thermal events affected the Craton along its boundary in Neoproterozoic times. One of these events was repeated hydrothermal activity along the Cafarnaum fault, a N-S-striking, 170 km long, strike-slip fault that juxtaposes Neoproterozoic carbonate units and Mesoproterozoic siliciclastic-carbonate units in the northern part of the Craton.

Hydrothermal boiling and implosive brecciation occurred along the fault. Decompression and cooler conditions induced precipitation of hydrothermal minerals in N-W-striking dilational jogs, mainly flanking the northern and southern fault terminations. The hydrothermal fluid structures are composed of hydrothermal breccias close to the main fault zones and along dilational jogs. In addition, calcite veins in the host units away from the fault are also part of the hydrothermal system. Therefore, the geometry of faults at shallow crustal levels influences the location of hydrothermal deposits.

Based on isotopic geochemistry, we show that meteoric water was the main fluid source that percolated the sedimentary rocks of the Irecê Basin and the Cafarnaum fault zone. Fluid inclusions in carbonate veins from the central part of the basin indicate a meteoric fluid with a δD value near -45‰ and a $\delta^{18}O$ value near -6.5‰. Temperature estimates based on the oxygen isotopic fractionation between the carbonate veins from the central part of the basin and the trapped fluid inclusions indicate temperatures ranging between 40 and 70°C. These temperature conditions agree with the lower $\delta^{18}O$ values of veins compared to the carbonate host rock. A similar $\delta^{18}O$ fluid value (-6.5‰) is obtained based on the interaction between these fluids and carbonates from the lower and upper parts of the succession.

In contrast, carbonates at the front edges of the basin associated with the Cafarnaum fault exhibit much lower $\delta^{18}O$ values, indicating higher crystallization temperatures. These carbonates are also associated with base metals and silica-rich fluids, suggesting that the fault behaved as a conduit for deeper fluid circulation in the basement. The mineral paragenesis (e.g., galena, sphalerite, barite, chlorite, illite, and quartz) and brecciated features associated with the veins and fault support this interpretation.

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Figure 1

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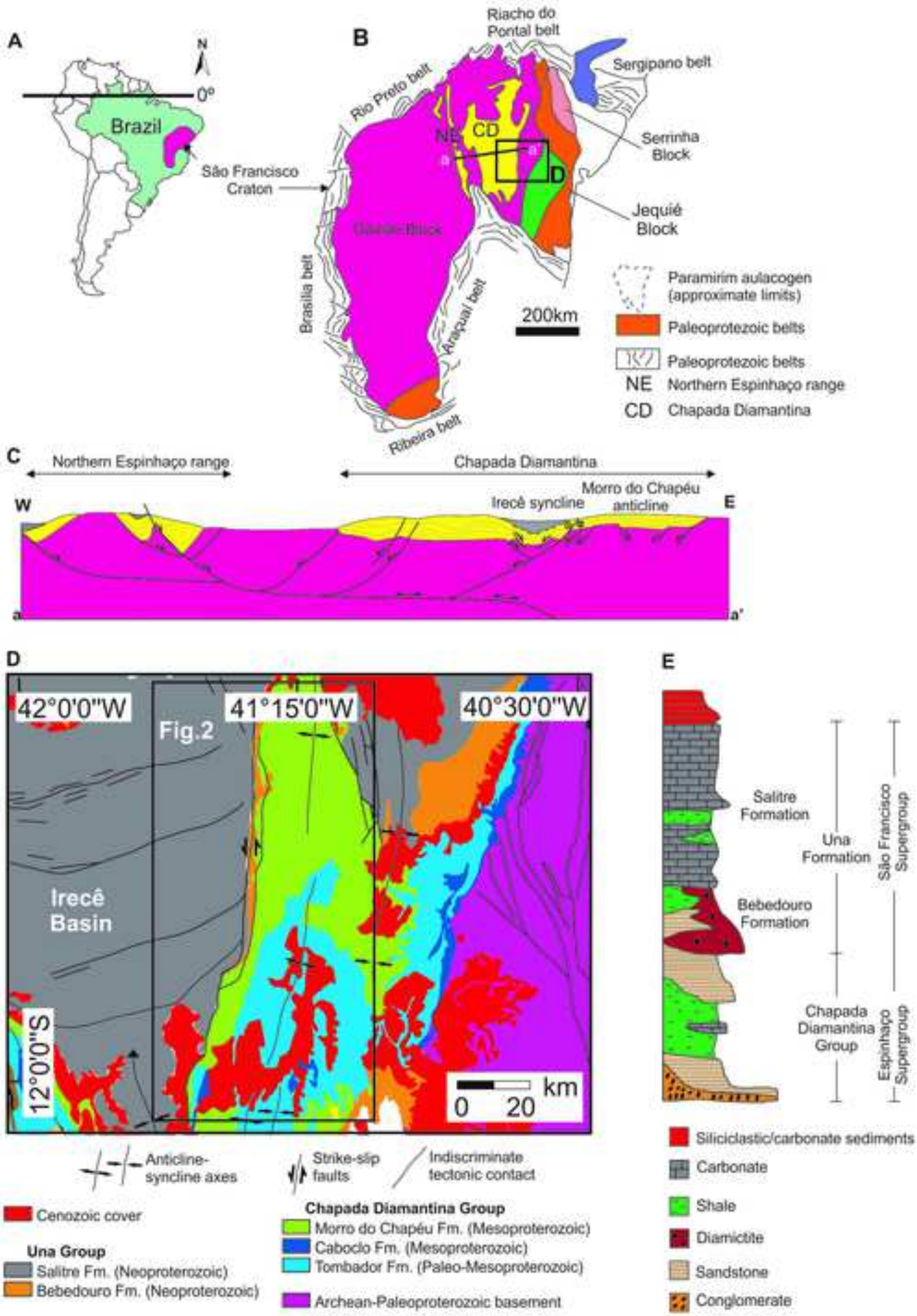

Figure 2

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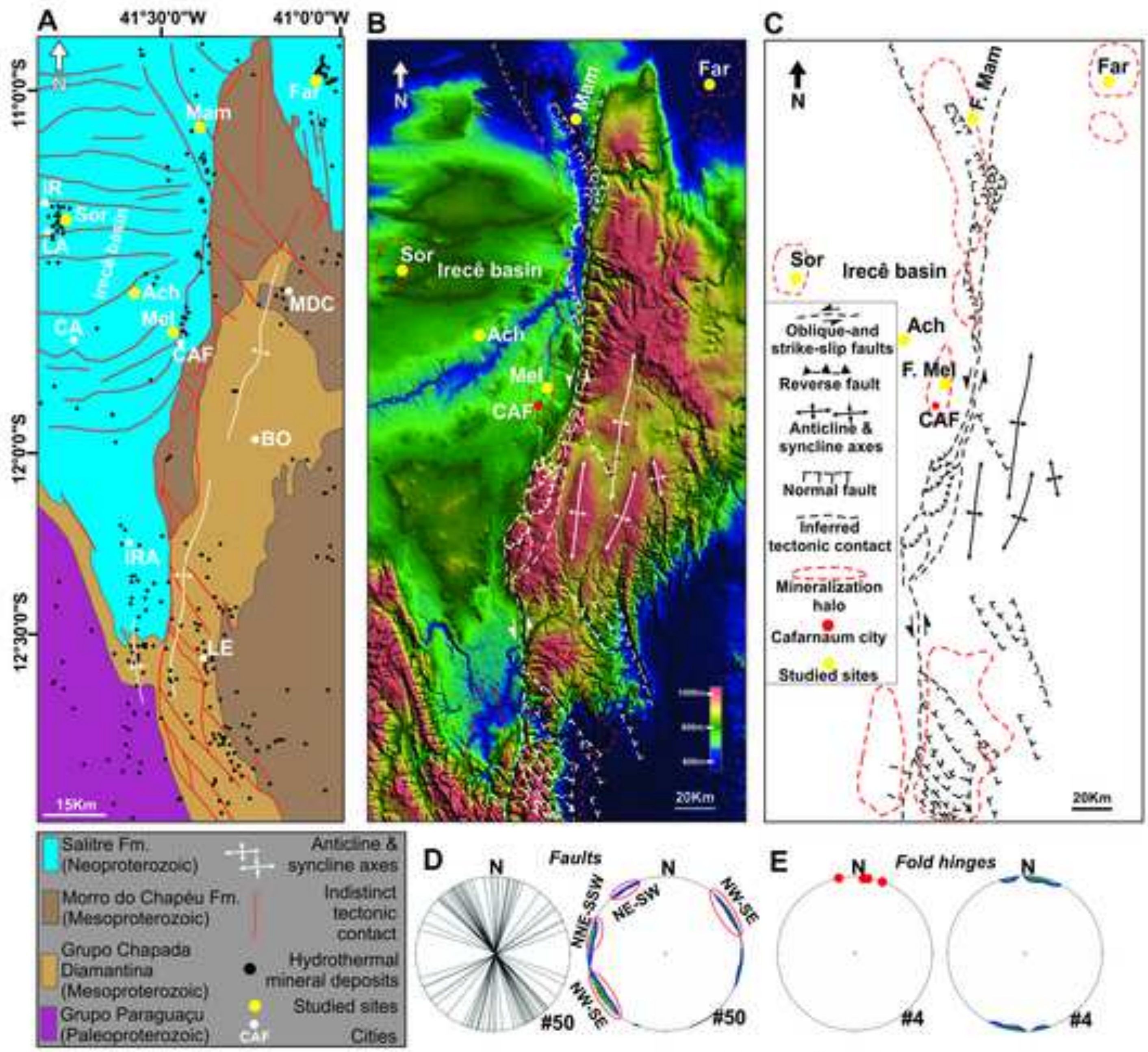

Figure 2. (A) Simplified geological map modified after *Levantamento Aerogeofísico da Área de Centro Norte Bahia - CBPM, 2011/12 Geologia - Mapa Geológico do Estado da Bahia - CBPM/CPRM, 2003.* (B) Structural framework of the study area superposed on ALOS PALSAR imagery. Dashed lines represent the inferred faults. Continuous white lines represent both anticline and syncline axes. (C) Line drawing of the structural framework presented in B. (D) Lower hemisphere equal-area projections of great circles representing the attitude of the documented faults and equal-area projection/density contour plots of the poles of the measured faults. (E) Lower hemisphere equal-area projections of fold hinges and relative density contour plots. (the map location can be found in Fig. Geological map).

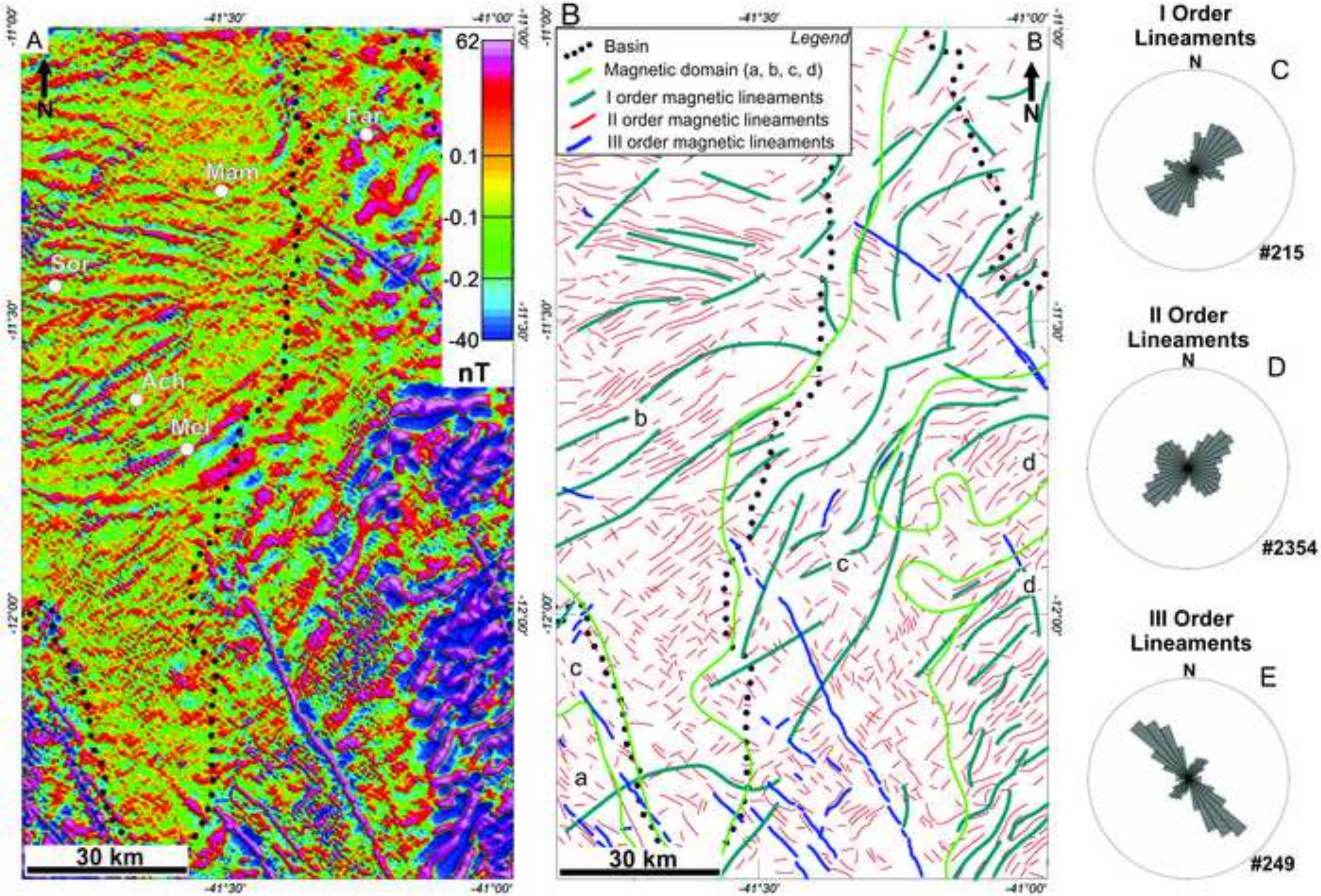

Figure 3. Behavior of magnetic lineaments in the study area: (A) Map of first derivate. (B) Lineaments Line drawing of the map presented in A. (C-D-E) Rose diagram representing the attitude of the documented first, second and third order lineaments.

Figure 4 Click here to access/download;Figure;Fig.4.jpg

Figure 4. (A) Outcrop view of subvertical bed layers in the Achado outcrop; (B) Close up view of a bed parallel slip surface. Kinematic indicators, such as striae are visible along the slip surface. (C) Close up view of a large bed parallel vein and bed perpendicular fractures; (D) Close up view of bed parallel veins and bed perpendicular fractures and veins. (E) Rose diagramm of the documented fractures in the Ach outcrop. (F) Lower hemisphere equal area projection of veins measured in the Ach outcrop. (G) and (H) Rose diagramm of the documented fractures and veins in the Far and Sor outcrops. See Fig. 2 for outcrops location.

Figure 5 Click here to access/download;Figure;Fig.5.jpg

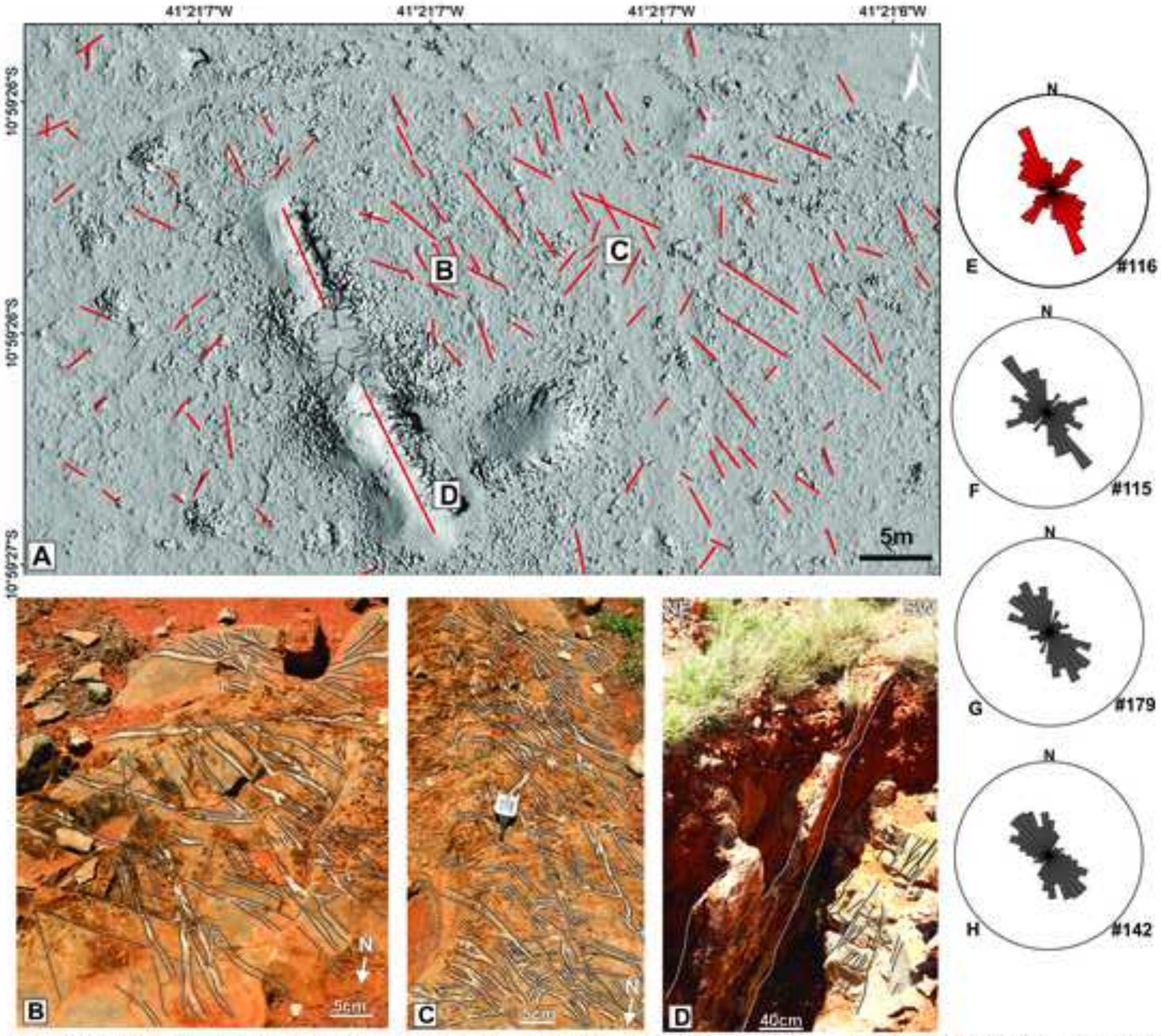

Figure 5. (A) Digital elevation model (DEM) of the Mamonas outcrop (outcrop localization in fig. 2: Mam). Red lines are associated to the structural lineaments; (B)(C) Outcrop view of veins and fractures. (D) Outcrop view of a large vein located in a fault damage zone. (E) Rose diagramm of the identified structural features from the DEM in Fig. 5a; (F) Rose diagramm of the documented veins and fractures displayed in Fig. 5b; (G) Rose diagramm of the documented veins and fractures displayed in fig. 5c; (H) Rose diagramm of the documented veins and fractures displayed in fig. 5d. See Fig. 3 for outcrops location.

Figure 6 Click here to access/download;Figure;Fig.6.jpg

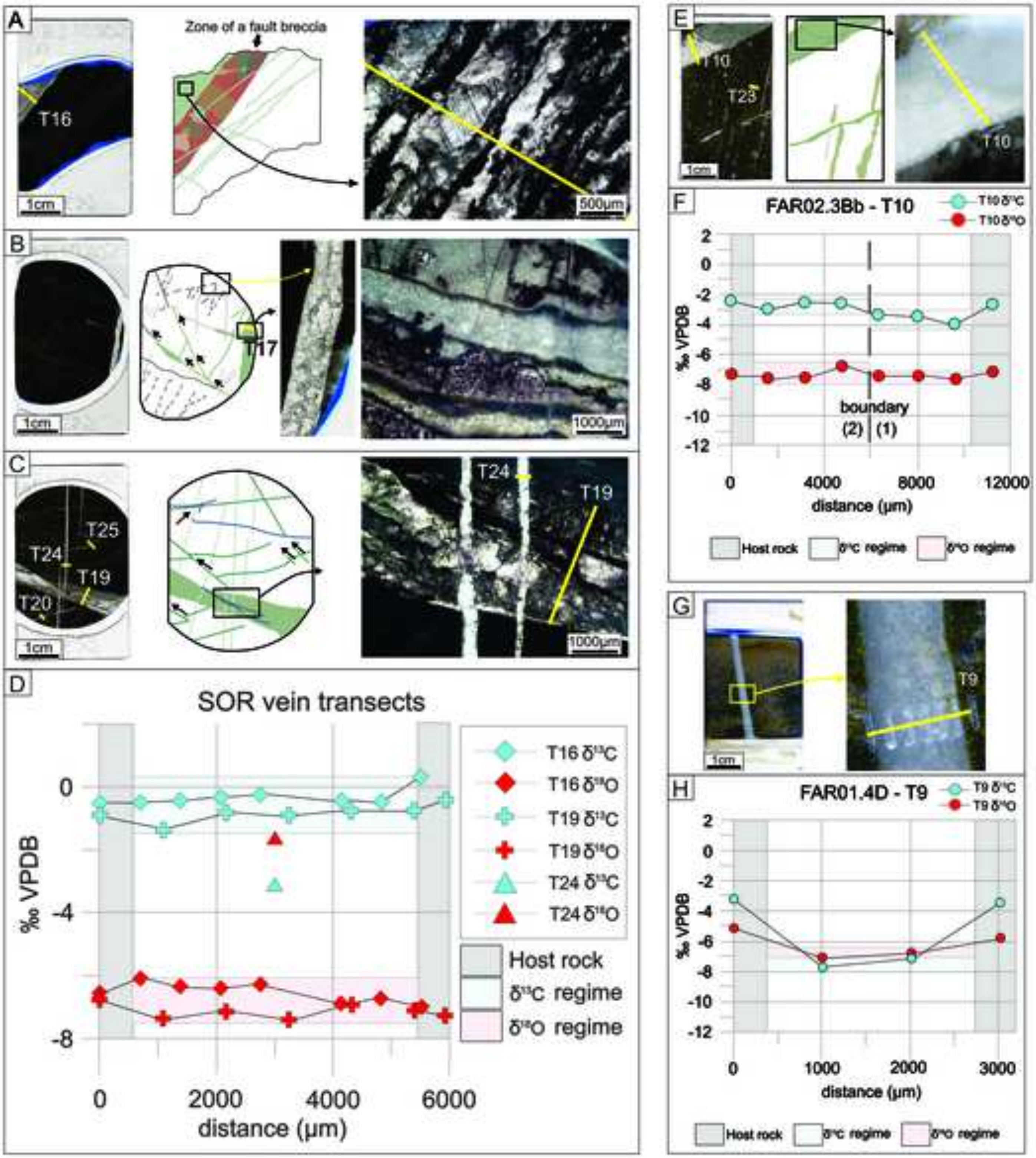

Figure 6. A) On the left, thin section SOR01.2Aa. On the center graphical representation of SOR01.2Aa with veins in green and fault breccia in multicolor. On the right, zoom in on sheeted character of vein T16. B) On the left, thin section SOR01.2Ab. On the center graphical representation of SOR01.2Ab. On the right zoom in on bedding parallel stylolites and NNE-SSW fractures. C) On the left, thin section SOR01.3Aa. On the center Micro map of all present features. On the right, crosscutting of shear fracture T19 and N-S vein T24. D) Stable isotope transects of T16,T19 and T24. E) Thin section FAR02.3Bb. On the center, graphic representation of thin section. On the left, zoom in on transect T10 across two calcite phases including crystallization.F) Transect T10. G) Thin section FAR014D, and zoom in on vein T9 with sampling location including crystallization. H) Transect T9.

Figure 7

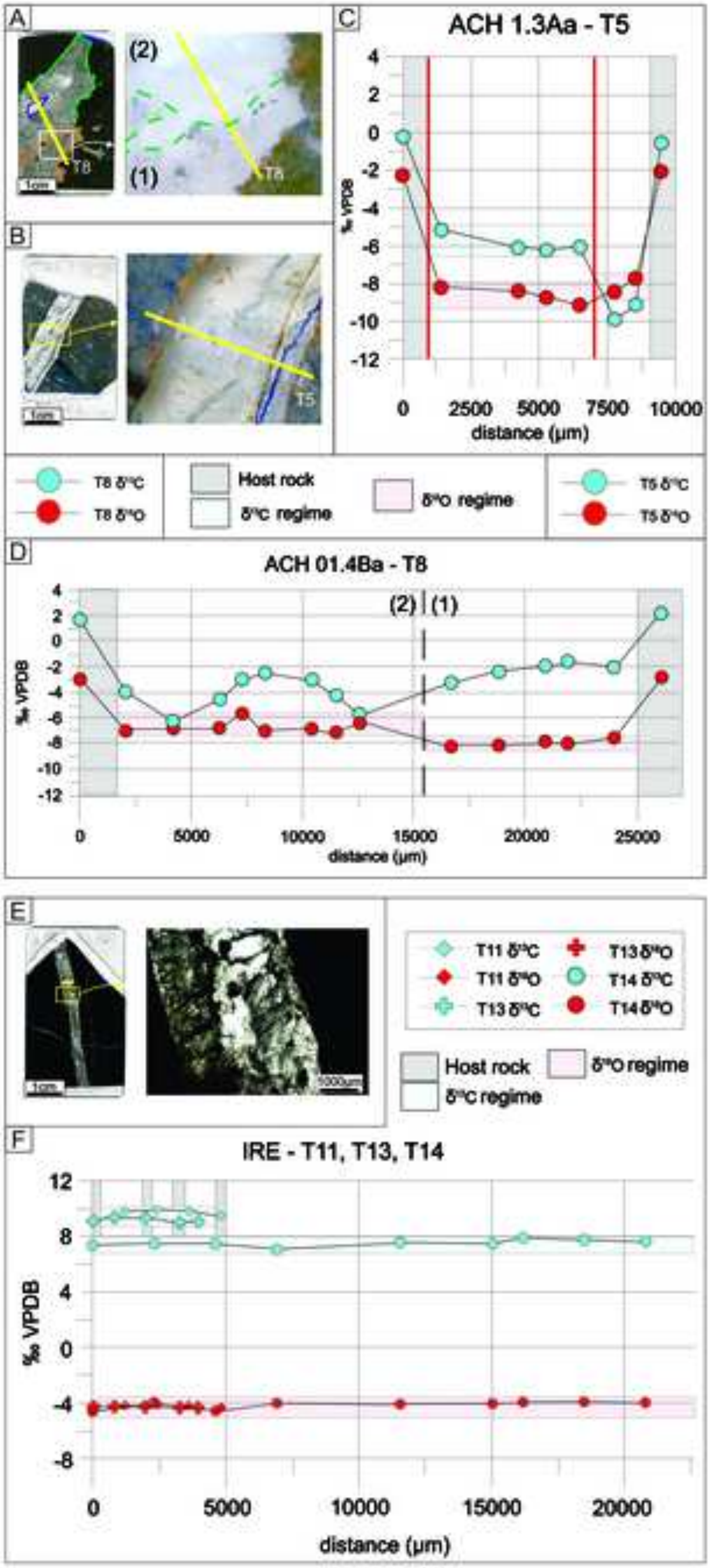

Figure 7. A) Thin section ACH01.4Ba with T8 location and two zones and, zoom in on zone boundary between (1) no host rock remnants and (2) with host rock remnants B) Thin section ACH01.3Aa and, zoom in on transect T5. C) Transect T5. The red lines mark a change in $\delta^{13}C_{VPDB}$ and a new growth plane. D) Stable isotope transect of T8. Note the difference in $\delta^{18}O$. E) Thin section IRE01.2Aa. and, zoom in on vein infill with needle shaped aragonite remnants. F) Stable isotope transects of vein T11, T13 and T14 from IRE. Host rock and vein infill have an almost identical isotope composition.

Figure 8 Click here to access/download;Figure;Fig.8.jpg

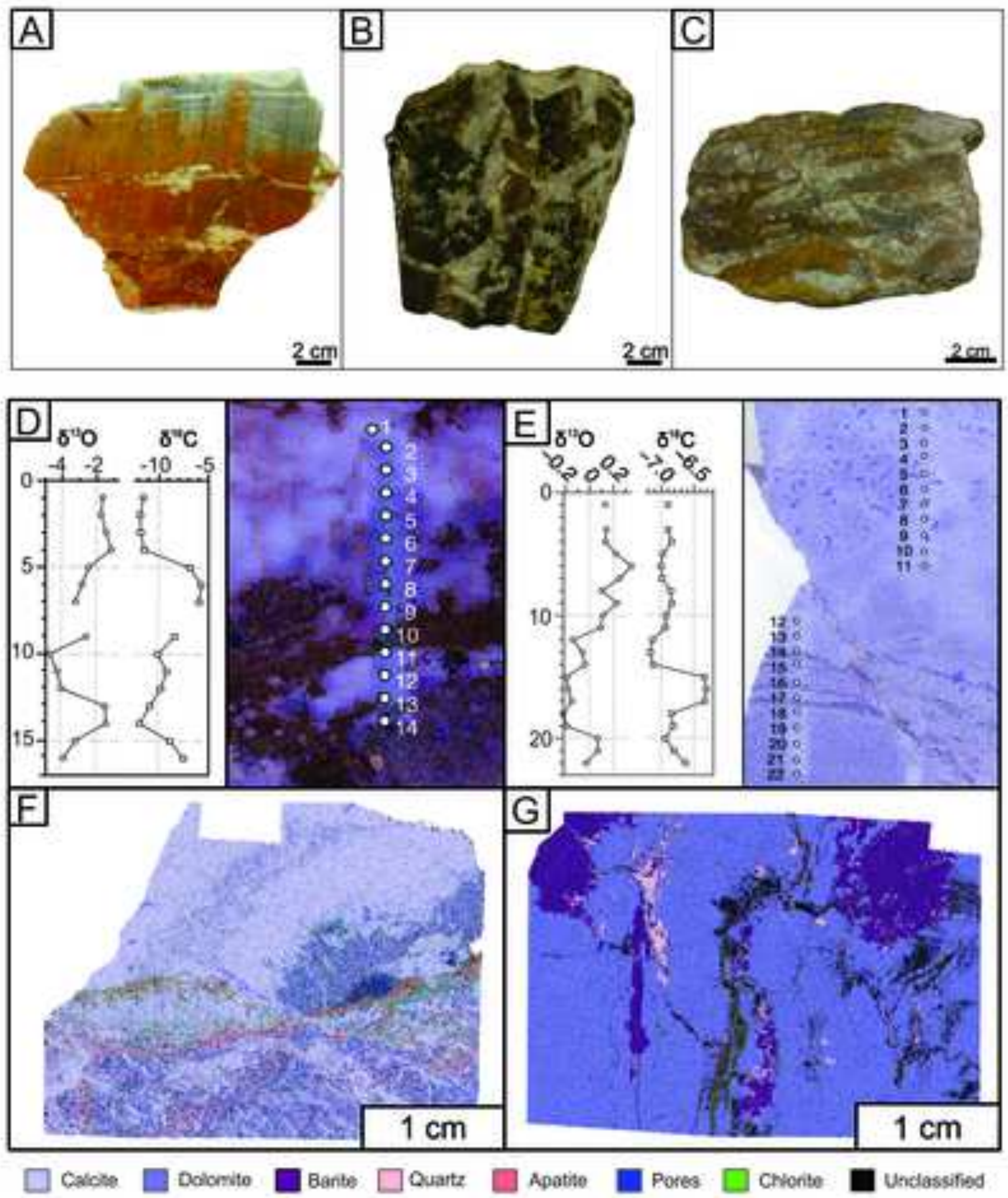

Figure 8. Samples from Melancias area showing the effects of hydrothermal alteration and hydraulic fracturing. A) Carbonate that shows partially preserved primary features grading to a brecciated zone. In the lower part of the sample, the primary features were obliterated by the hydrothermal alteration. B)Vein of carbonate by sucessive precipitation of carbonate and Fe-rich zones. C) Hydralic breccia with clasts of the primary carbonate. D) and E) Thin section from Melancias in which calcite is the main mineral. The diagram also presents $\delta^{13}C$ and $\delta^{18}O$ across profiles. F) and G) QemScan image of samples from Melancias showing the hydrothermal mineralogy made of barite, quartz, illite, and chlorite. Note that these mineras concentrate along fractures.

Figure 9 Click here to access/download;Figure;Fig.9.jpg

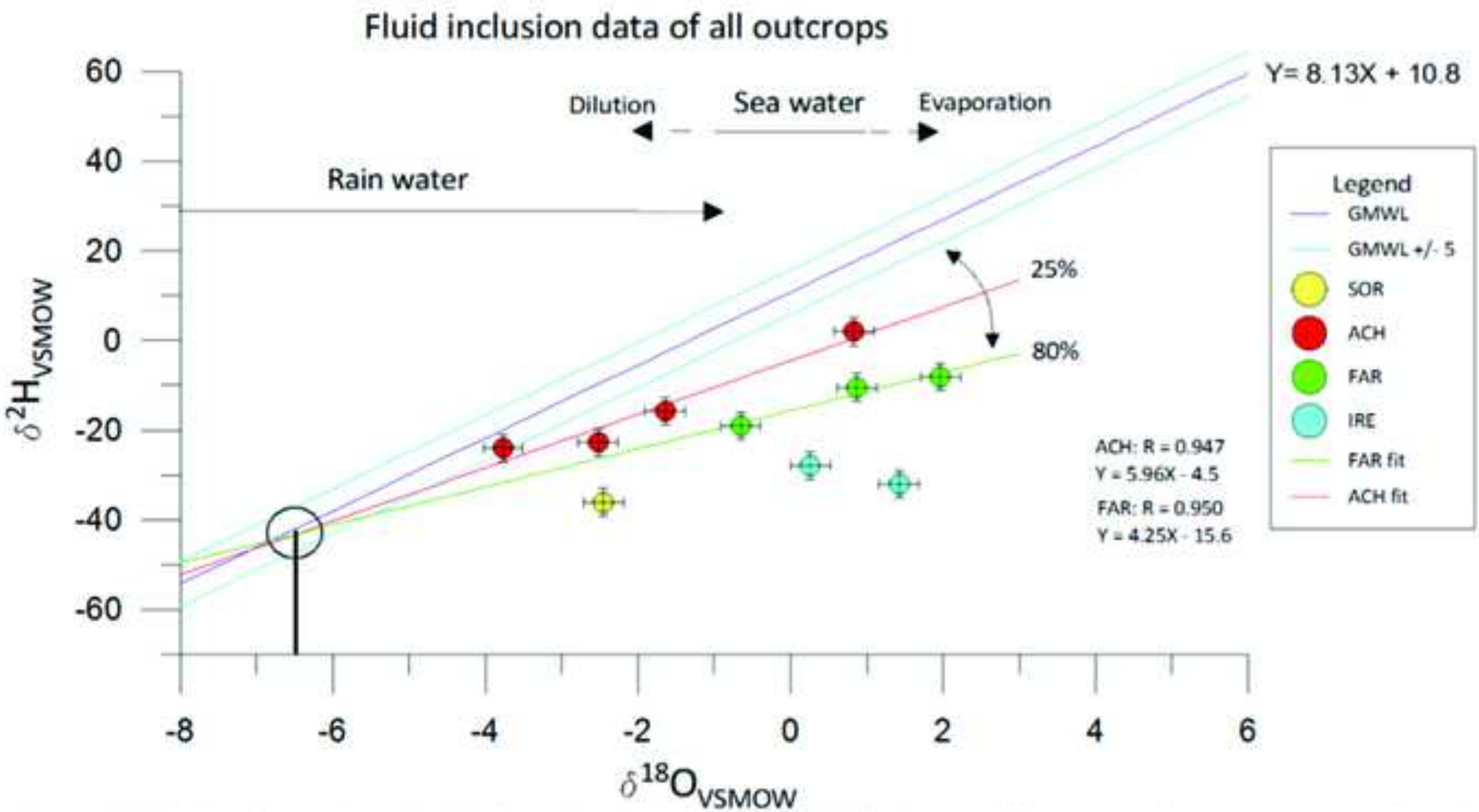

Figure 10. Fluid inclusion data GMWL based on Rozanski et al. (1993). Regions of marine and meteoric waters based on Moore (1989). Sample plot in both meteoric and marine domain. Trend lines of ACG and FAR cross the GMWL on the same point (~-6,5‰ for $\delta^{18}O_{VSMOV}$; -45‰ for δD_{VSMOW}).

Figure 10

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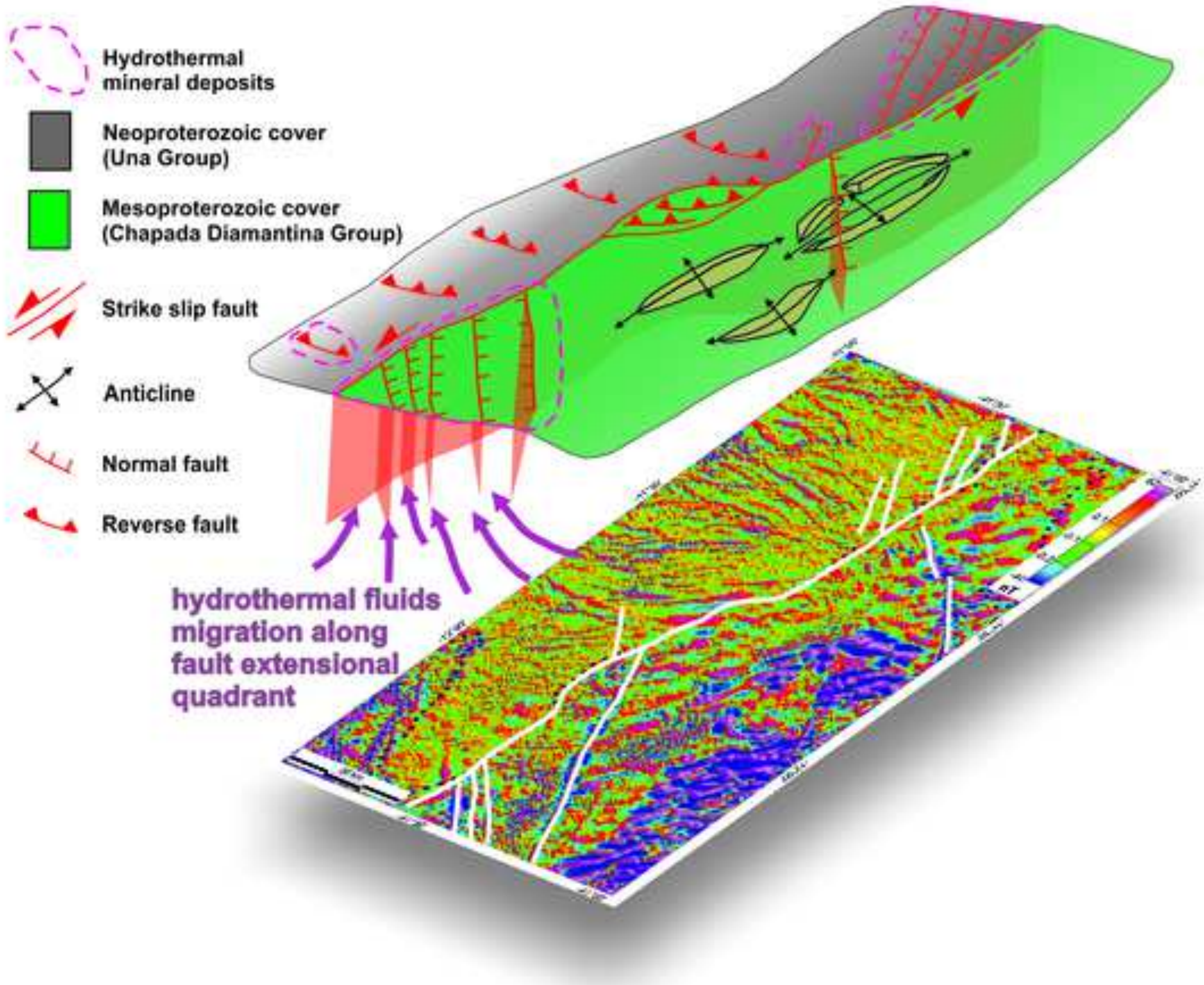

Figure 10. Conceptual model proposed for the study area. Cartoon displaying the current regional scale configuration and the connection with the deep magnetic lineaments.

Figure 11

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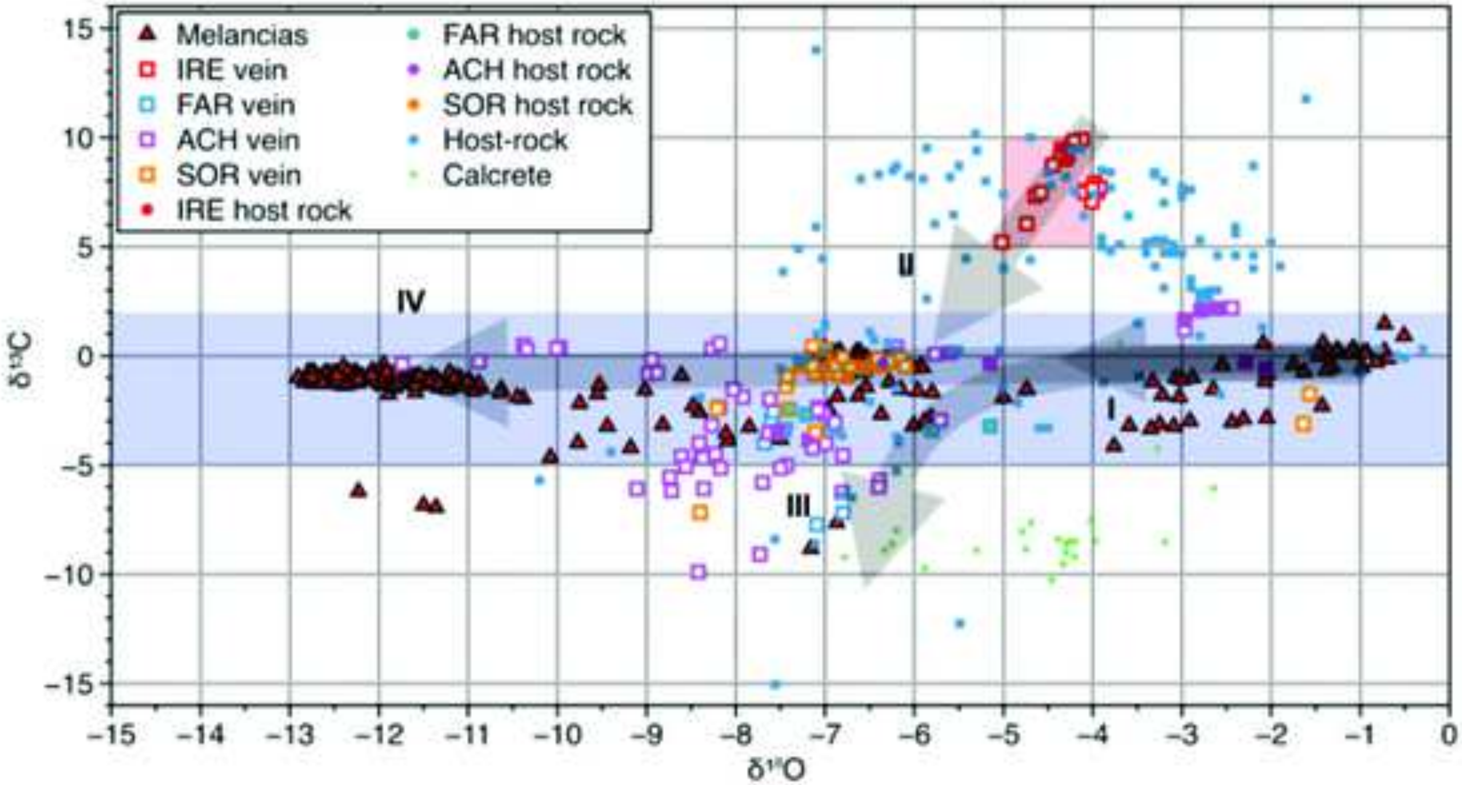

Figure 11. Carbon and oxygen isotopes of samples from the central part of the basin (IRE, FAR. ACH, and SOR) and samples from the Melancias outcrop compared to other published isotope data from the basin. This plot shows different scenarios of isotope evolution: I. Interaction between meteoric fluid and carbonates of the lower stratigraphic section; II. Interaction between meteoric fluid and carbonates of the upper stratigraphic section; III. Low $d^{13}C$ carbonates related to the same fluids responsible for calcrete formation in the area; IV. Carbonates formed by high-temperature fluids that interacted with deep-crustal levels. Host-rock data (Misi and Kyle, 1994; Misi and Veizer, 1998; Borges et al., 2016; Caird et al., 2017); Calcrete data (Borges et al., 2016; Caird et al, 2017).

Table 1: Isotopic composition of carbonates from central part of the basin. IRE; ACH; SOR; FAR. V refers to vein, HR to host-rock, and BREC to breccia.

Achado - ACH				Fazenda Arrecife - FAR				Irecê - IRE				Soares - SOR			
Sample	$\delta^{13}C$	$\delta^{18}O$	V/HR	Sample	$\delta^{13}C$	$\delta^{18}O$	V/HR	Sample	$\delta^{13}C$	$\delta^{18}O$	V/HR	Sample	$\delta^{13}C$	$\delta^{18}O$	V/HR
T3	0.1	-5.6	HR	T9.1	-3.2	-5.2	HR	T11.3	9.8	-4.2	V	T16.1	-0.9	-6.8	HR
T3.2	-4.5	-8.2	V	T9.3	-7.7	-7.1	V	T11.5	9.9	-4.1	V	T16.3	-1.4	-7.4	V
T3.3	-5.2	-7.5	V	T9.5	-7.2	-6.8	V	T11.7	9.8	-4.2	V	T16.5	-0.8	-7.1	V
T3.4	-5.6	-8.7	V	T9.7	-3.4	-5.8	HR	T11.9	9.5	-4.4	HR	T16.7	-0.9	-7.4	V
T3.5	-4.6	-8.6	V	T10.1	-2.5	-7.4	HR	T13.1	9.2	-4.3	HR	T16.9	-0.7	-6.9	V
T3.6	0.1	-5.8	V	T10.3	-3.0	-7.6	V	T13.2	9.4	-4.3	V	T16.11	-0.8	-7.1	V
T4.1	-0.3	-5.2	HR	T10.5	-2.6	-7.6	V	T13.3	9.3	-4.3	HR	T16.12	-0.4	-7.3	HR
T4.2	-0.3	-6.4	HR	T10.7	-2.6	-6.9	V	T13.4	9.0	-4.3	HR	T17.1	0.4	-7.1	V
T4.3	-3.9	-7.2	HR	T10.9	-3.4	-7.5	V	T13.5	9.1	-4.4	V	T17.3	-2.4	-8.2	V
T4.4	-3.4	-7.5	HR	T10.11	-3.5	-7.5	V	T14.1	7.3	-4.6	V	T17.5	-0.1	-6.2	V
T4.5	-0.3	-10.9	V	T10.13	-4.0	-7.7	V	T14.3	7.5	-4.0	V	T19.1	-0.5	-6.6	HR
T4.6	0.4	-10.0	V	T10.15	-2.7	-7.2	HR	T14.5	7.5	-4.6	V	T19.2	-0.5	-6.1	V
T4.7	-0.8	-9.0	V					T14.7	7.1	-4.0	V	T19.3	-0.4	-6.4	V
T4.8	-0.4	-11.7	V					T14.9	6.1	-4.7	V	T19.4	-0.3	-6.4	V
T4.9	0.5	-10.4	V					T14.11	7.6	-4.1	V	T19.5	-0.3	-6.3	V
T4.10	0.3	-10.3	V					T14.13	5.2	-5.0	V	T19.7	-0.5	-6.9	V
T4.12	0.3	-10.0	V					T14.14	7.5	-4.1	V	T19.8	-0.5	-6.7	V
T4.13	0.6	-8.2	V					T14.15	7.9	-4.0	V	T19.9	0.3	-7.0	HR
T5.1	-0.3	-2.3	HR					T14.17	7.7	-3.9	V	T24.1	-3.1	-1.6	V
T5.2	-5.1	-8.2	V					T14.19	7.7	-4.0	V				
T5.4	-6.1	-8.4	V					T12.1	8.7	-4.5					
T5.5	-6.2	-8.7	V												
T5.6	-6.1	-9.1	V												
T5.7	-9.9	-8.4	V												
T5.8	-9.1	-7.7	V												
T5.9	-0.6	-2.1	HR												
T6.1	2.2	-2.6	HR												
T6.2	-4.7	-8.4	V												
T6.3	-5.1	-8.6	V												
T6.5	-2.7	-7.0	BREC												
T6.6	1.2	-3.0	BREC												
T6.7	-2.4	-7.1	BREC												
T6.8	2.2	-2.4	BREC												
T8.1	1.6	-3.0	HR												
T8.3	-4.0	-7.0	V												
T8.5	-6.3	-6.8	V												
T8.7	-4.6	-6.8	V												
T8.8	-3.0	-5.7	V												
T8.9	-2.5	-7.1	V												
T8.11	-3.0	-6.9	V												
T8.12	-4.2	-7.1	V												
T8.13	-5.7	-6.4	V												
T8.17	-3.2	-8.3	V												
T8.19	-2.4	-8.2	V												
T8.21	-1.9	-7.9	V												
T8.22	-1.5	-8.0	V												
T8.24	-2.0	-7.6	V												
T8.26	2.1	-2.8	HR												

Table 2: Isotope data from fluid inclusions of carbonates from the central part of the basin. The temperature was calculated based on the oxygen isotopic composition of calcite and fluid, according to Kim & O'Neil (1997).

Sample	Location	Fluid δD_{SMOW}	Fluid $\delta^{18}O_{SMOW}$	Calcite $\delta^{18}O_{PDB}$	Calcite $\delta^{18}O_{SMOW}$	T in C
ACH01.2Bb T4-1	ACH	-22.7	-2.5	-7.4	23.3	39
ACH01.2Bb T4-2	ACH	-24.0	-3.8	-10.1	20.5	47
ACH01.3Aa T5-1 (left)	ACH	1.9	0.8	-8.6	22.1	66
ACH01.4BaT8-1 (grey)	ACH	-15.7	-1.6	-8.0	22.7	48
IRE01.2Aa T11	IRE	-32.0	1.4	-4.2	26.6	43
IRE01.3Ba T14	IRE	-27.9	0.3	-4.1	26.6	37
SOR01.3Aa T19	SOR	-36.0	-2.5	-6.5	24.3	35
FAR01.4D T9	FAR	-10.5	0.9	-7.0	23.7	56
FAR02.3Bb T10-1 (milky, right)	FAR	-8.2	2.0	-7.6	23.1	67
FAR02.3Bb T10-2 (transparant, left)	FAR	-19.0	-0.7	-7.5	23.1	51