Conundrum of the iron isotopic fractionation: banded iron formation from Urucum district, West Brazil

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Purposes

- Analyze iron isotopic data in banded iron formation from the Urucum District (W Brazil), using statistics to test for anomaly fractionation;
- Determinate the post depositional influence within these rocks, using X-Ray Diffraction and diagenetic analyses in siliciclastic facies;
- Attempt to recognize the origin of the magnetite, using magnetic measurements.

Motivations

- Paleoclimatic variations, during the Precambrian, caused disturbances in the iron cycle which reacted by depositing paleoclimatic archives as banded iron formations (Young 2019; Campbell & Allen 2008; Summarized in the next two slides);
- Investigations on the iron cycle can shed a light on the responses of the ocean redox state and the iron reservoir through these atmospheric variations (Johnson et al. 2003);
- The analyses of the iron isotopic composition in the BIFs are a fundamental tool for these studies but it’s essential to considerate the associated isotopic fractionation processes and uncertainties during the interpretation of these data (Kunzmann et al. 2017);
- One question moves us: How significant was the enrolment of bacteria in the deposition of iron oxides?

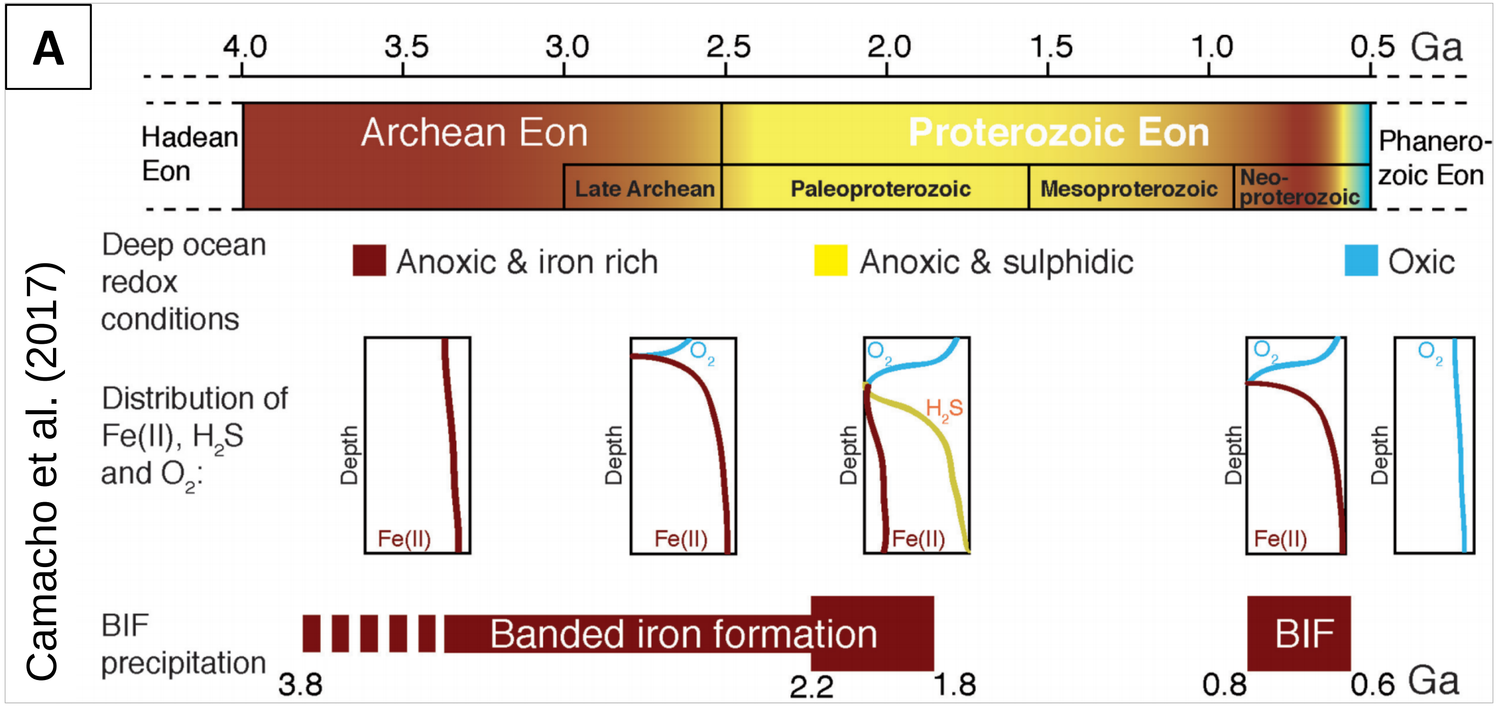
Climate system evolution

► Archean Eon (4.0 – 2.5Ga): CO_2-rich atmosphere; Anoxic Fe^{+2} rich ocean (fig.**A**); Complex paleogeogra-phic reconstructions.

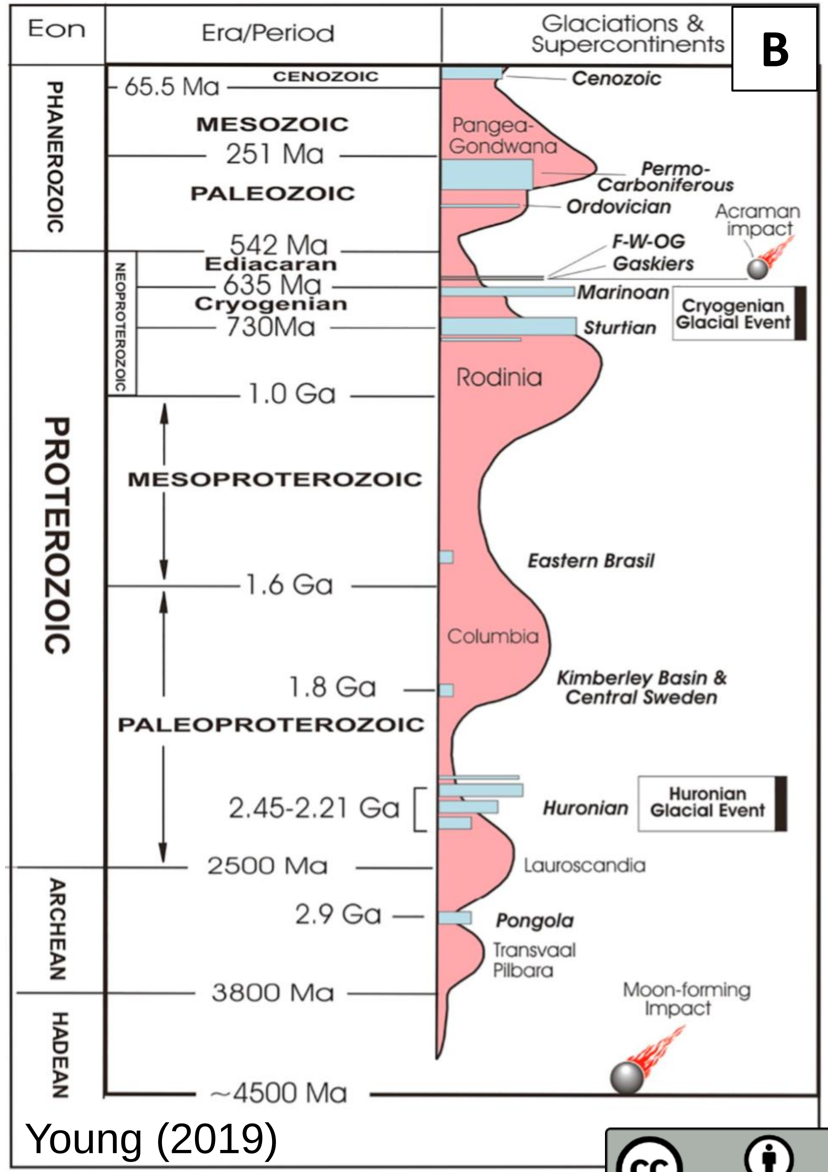
► Archean-Paleoproterozoic (~2.5Ga): *Great Oxidation Event*; Changes in the ocean redox-state (fig.**A**); Huronian glaciation (fig.**B**); Lauroscandia supercontinent in low latitudes (fig.**B**).

► Boring billion (1.8 – 0.8Ga): Climatic stability; Intense tectonic activity; No glaciations (fig.**B**).

► Neoproterozoic Era (1.0 – 0.541Ga): Neoproterozoic Oxidation Event; Deep ocean withferruginous anoxia (fig.**A**); Rodinia supercontinente (fig.**B**); Biological innovations; Glaciations Sturtian (~740–647Ma), Marinoan (~660–635Ma) e Gaskiers (~580Ma; fig.**B**));

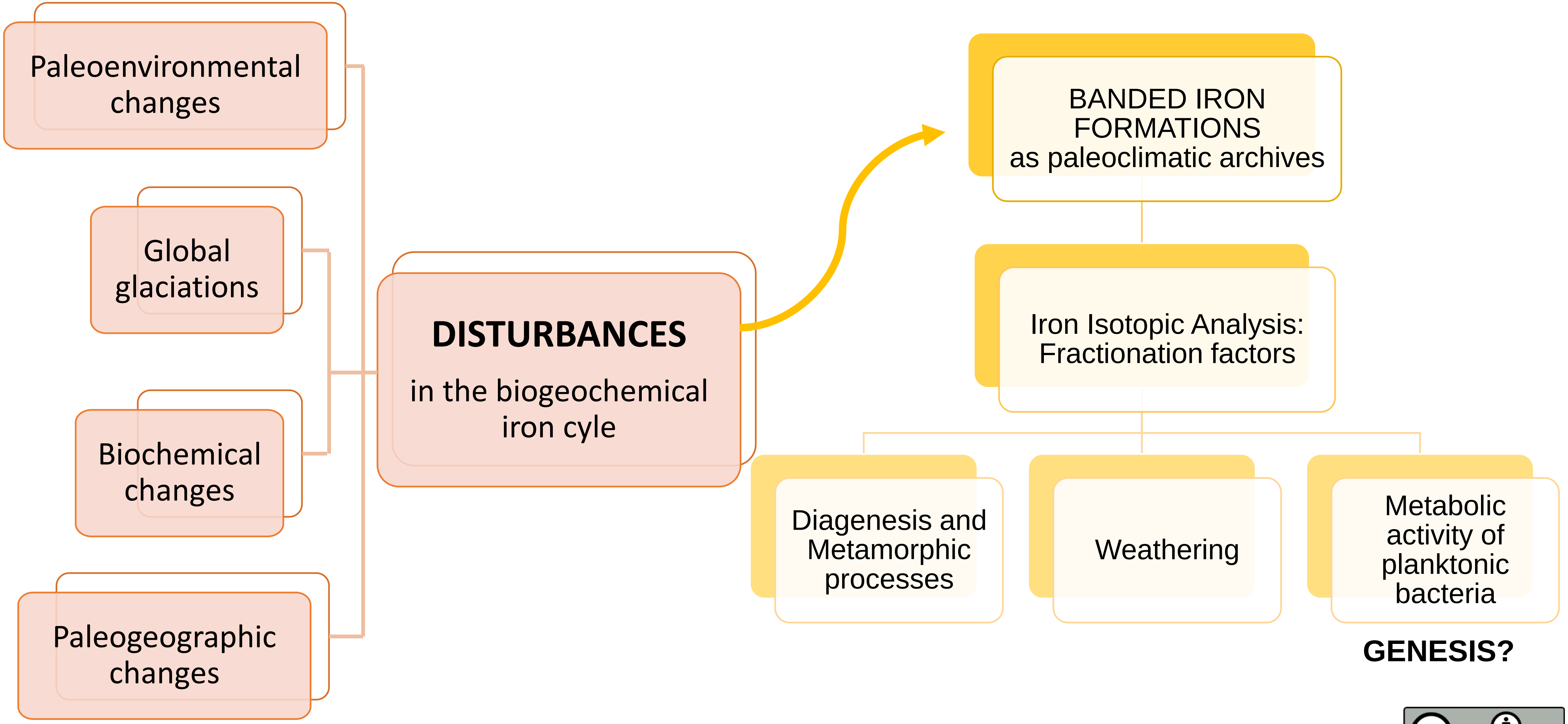


Camacho et al. (2017)

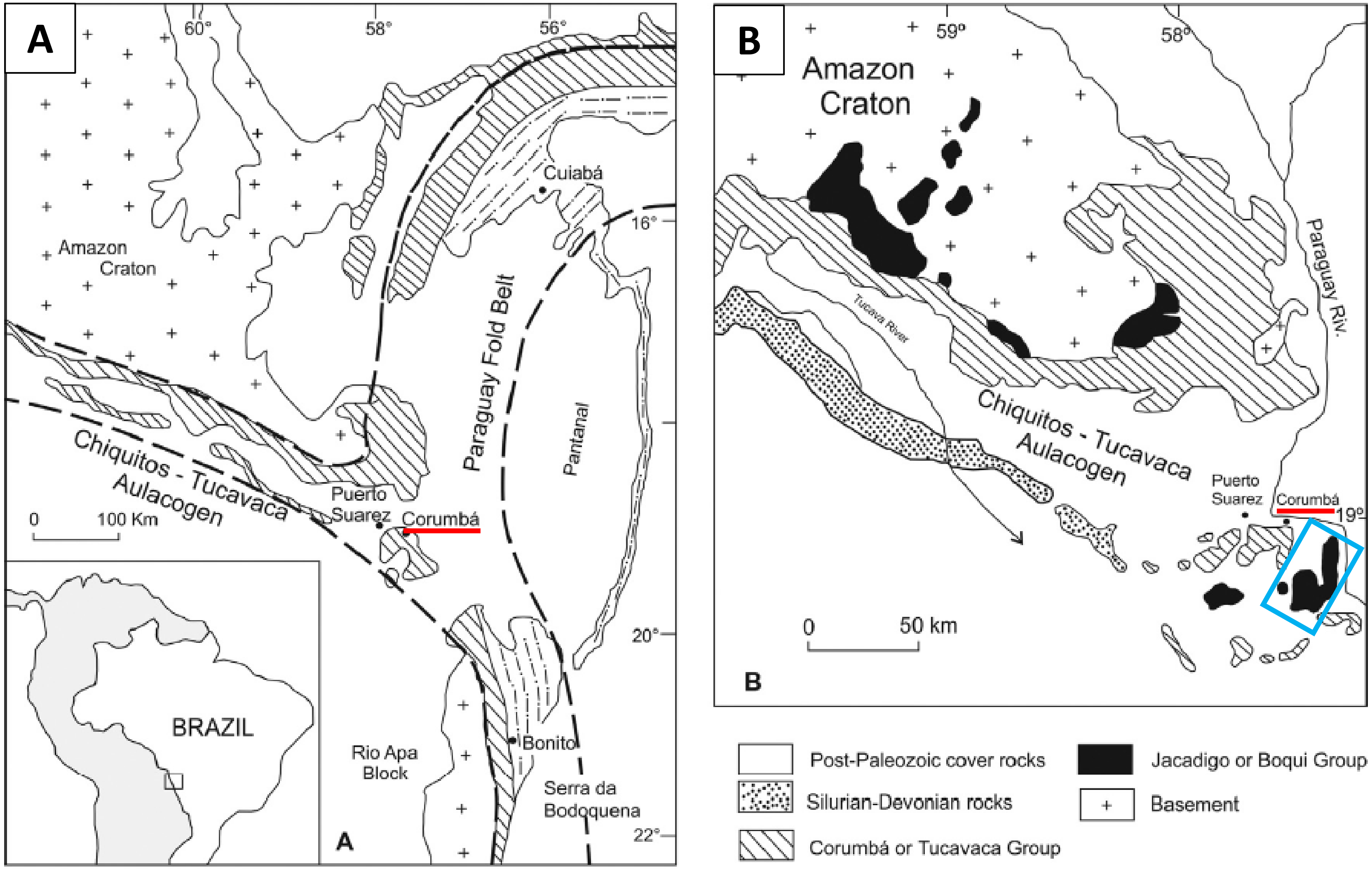


Young (2019)

Deposition of iron formations



Studied area: The Urucum District



Walde et al. (2015)

The Urucum district (blue rectangle in fig.**B**) is located near Corumbá city (marked red in figs.**A** and **B**), on the eastern edge of the Amazon craton – Rio Apa block. It is inserted in the Paraguay Belt, a late Pan-African-Brasiliano age fold belt (Angerer et al. 2016)

The commonly accepted tectonic environment for the Urucum district is a NE–SW striking graben structure in a compressive setting (Trompette et al., 1998).

Extensional tectonics, just before the Ediacaran Period, generated a graben system, the Corumbá graben (Jones 1985; Boggiani 1998, Trompette et al. 1998). This graben was first filled by the Jacadigo Group and the Puga Formation and, later on, by the Corumbá Group (Walde et al. 2015).

Samples

THREE DRILLCORES AT THE URUCUM DISTRICT:

- UR51;
- RK62;
- RK25.

Banda Alta Formation - **Jacadigo Group**

These drillcores display the following facies of the Banda Alta Formation:

- Jaspilites and Mn ore horizons;
- Hematitic and manganese-rich arkoses, diamictites, arkoses, siltstones.

Methods applied*:*

- *Iron isotopic analyses;*
- *X-Ray Diffraction;*
- *Kübler Index determination;*
- *Magnetic Mesurements.*

RK25-111,25-111,35 – diamicte

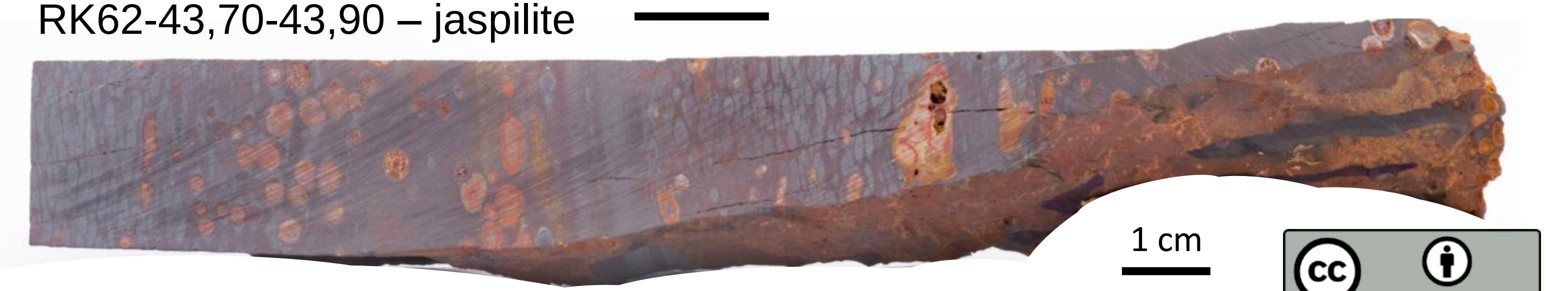
UR51-120,95-121,00
Mn horizont

1 cm

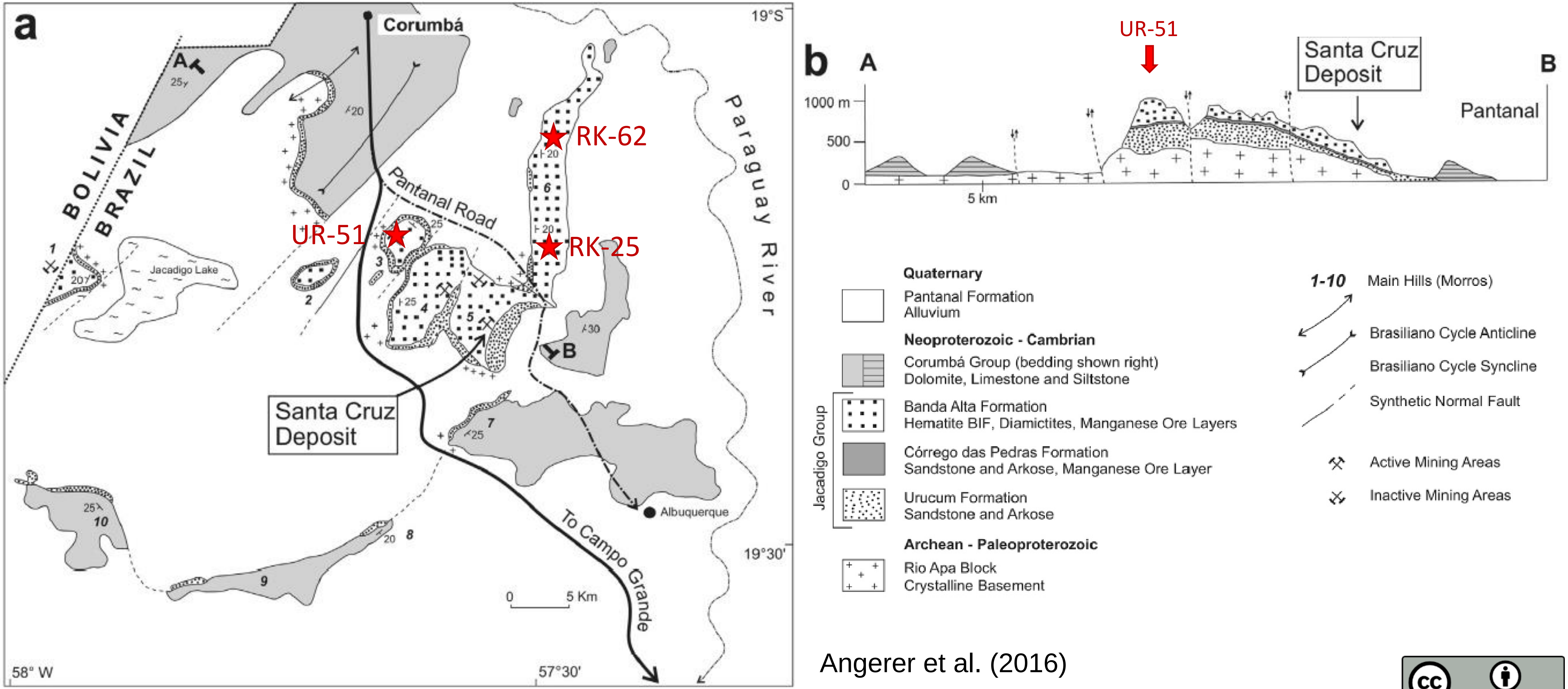
RK25-234,65-234,85
Askose

1 cm

RK62-43,70-43,90 – jaspilite

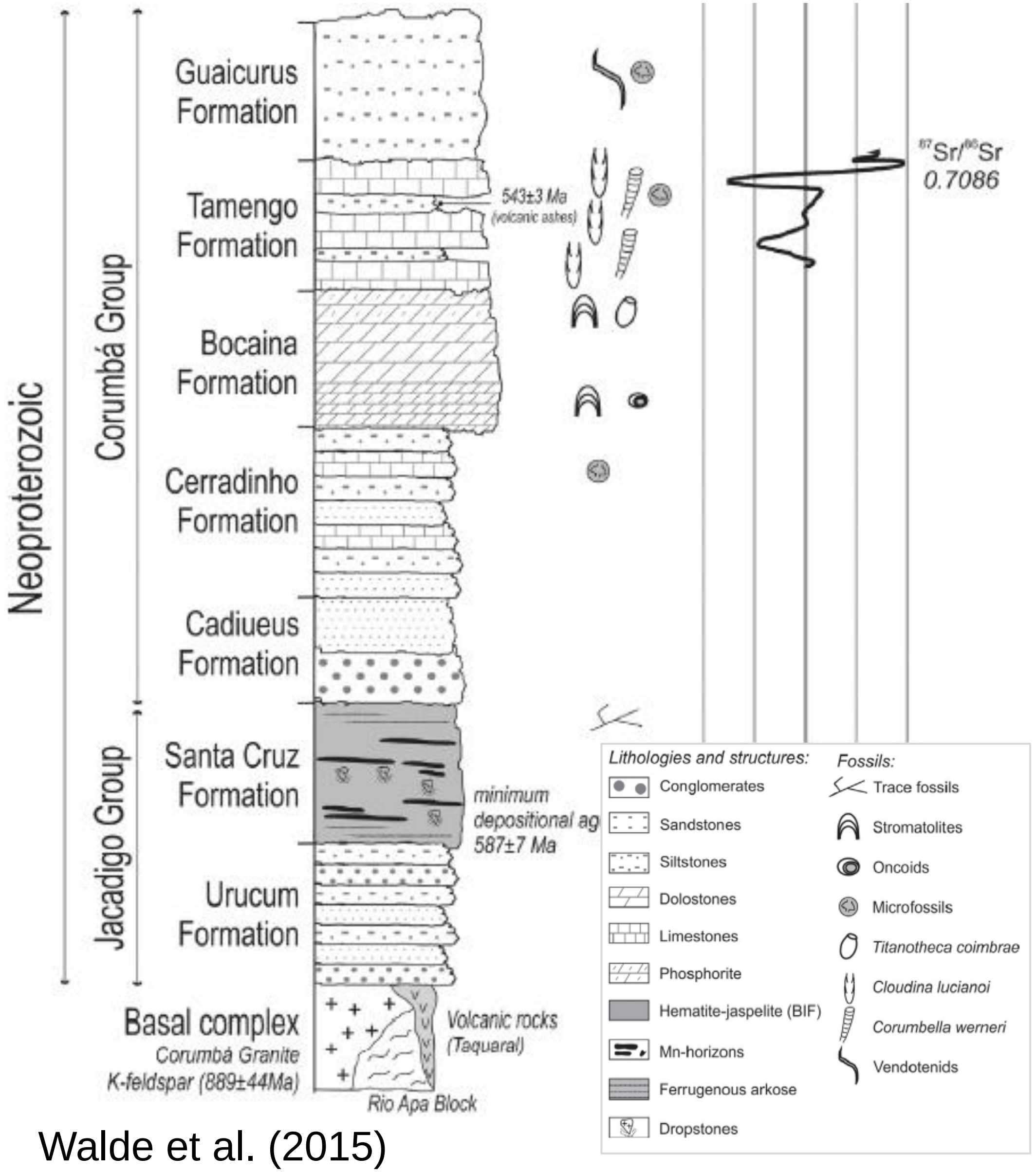


The Urucum District & drillcores locations



Angerer et al. (2016)

Age constrains – Jacadigo Group



Walde et al. (2015)

<u>LACKS UNEQUIVOCAL, DIRECT GEOCHRONOLOGICAL DATA</u>

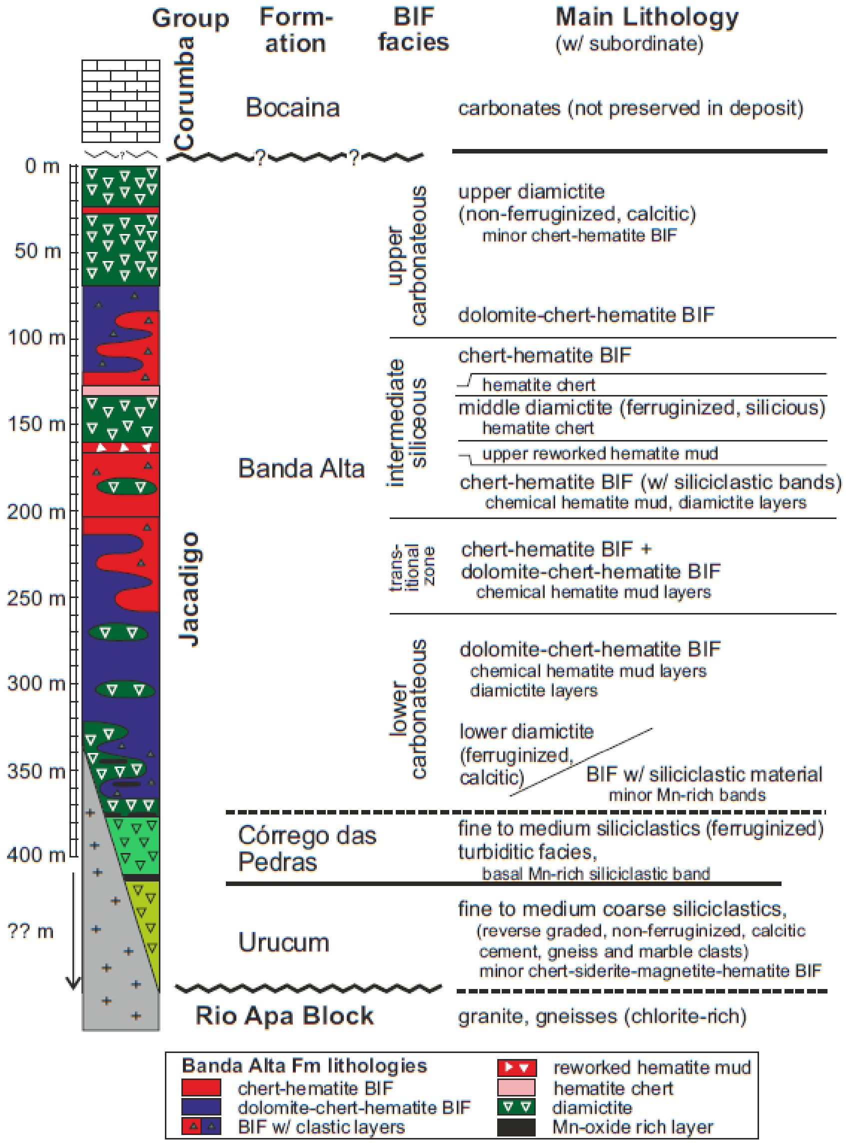
Basement granites have igneous K/Ar age of ca.889 ± 44 Ma (Hasui and Almeida, 1970)

Minimum age for the Jacadigo Group of 587 ± 7 Ma, by ^{40}Ar/^{40}Ar dating of diagenetic cryptomelane in the Mn-formation near the base of the Santa Cruz Formation (Piacentini et al., 2013).

Maximum depositional age of 695 ± 17 Ma by U-Pb zircon dating in the Santa Cruz Formation (Frei et al., 2017).

The Jacadigo Group was more likely related to the Cryogenian Sturtian or Marinoan events than to the 580-million-year-old Gaskiers glaciation.

Jacadigo Group’s lithostratigraphy and drillcores sytratigraphy

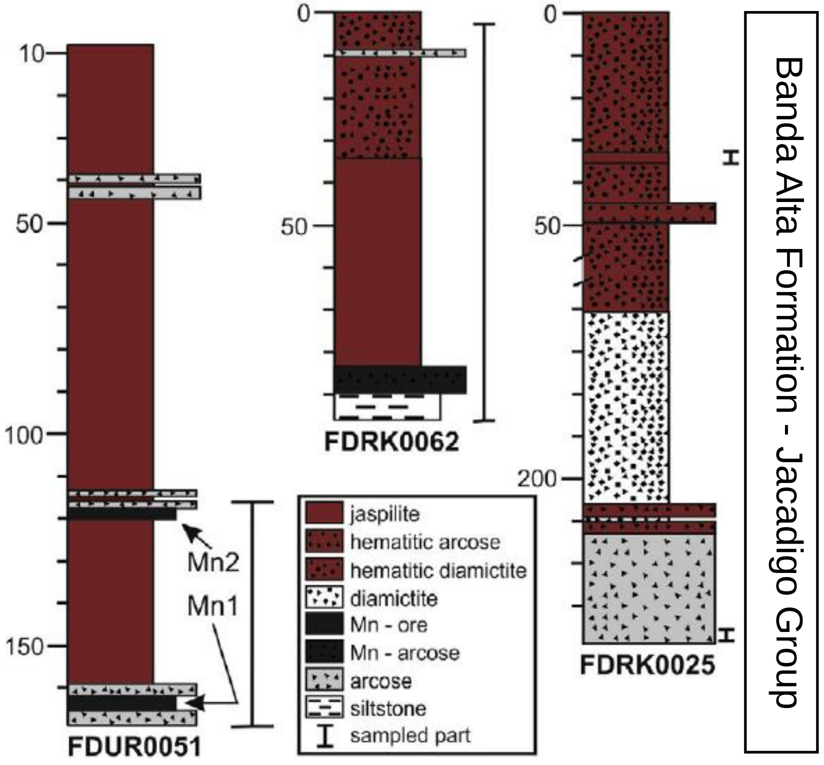


Angerer et al. (2016)

The samples analyzed in this research were previously published by Viehmann et al (2016), collected in the mining area of Vale Company at the Urucum District.

Drillcore UR51 is located in the Serra do Urucum and encounters Mn ore horizons Mn1 and Mn2, jaspilites and arkoses.

Drillcores RK25 and RK62 are located in the eastern Serra do Rabicho. Both of them encountered hematitic and manganese-rich arkoses, diamictites, arkoses, siltstones and jaspilites.



Viehmann et al. (2016)

Methods

IRON ISOTOPIC ANALYSES

Initially, the samples were sprayed. Later on, they were subjected to the digestion process that consist in a sequence of hydrofluoric acid, nitric acid and hydrochloric acid attack and heating procedures. The purification was performed by ion chromatography on heat-shrinkable Teflon columns filled with anionic resin (Bio-Rad AG1 X4, 200-400 mesh).

The iron isotopic analyses were performed by the Thermo-Finnigan Neptune inductively coupled plasma mass spectrometer. Between each analysis, the international iron isotopes reference material (IRMM-14) was analyzed under the same analytical conditions.

All these procedures were performed in the Geochronological Laboratory at the University of Brasilia (Brasília-Brazil).

STATISTIC ANALYSES

We have performed a statistic description of a **bulk** iron isotopic compilation from BIFs of different localities through the Precambrian, highlighting the Archean (4.0 – 2.5Ga), the Paleoproterozoic (2.5 – 1.0Ga) and the Neoproterozoic (1.0 – 0.541Ga).

Using this statistic description, we evaluate the iron isotopic data of the Neoproterozoic BIF of Banda Alta Formation (Jacadigo Group), from the Urucum district, testing for anomalies values using F test, T test and ANOVA test.

Methods

X-RAY DIFFRACTION

Sample preparation initially included material disaggregation with a hammer and powdering in the Planetary Mill *pulverisette* by Fritsch, for 5 minutes with 400 rpm. X-ray powder diffraction was performed on whole rock samples, as well as on clay fractions.

Analyses were performed in a RIGAKU Ultima IV diffractometer equipped with CuKa radiation, Ni filter, under 35 kV and 15 mA. The samples were scanned at 5º/min velocity. Mineral phases were identified using Jade XRD 9.0 (Materials Data) with PC-PDF (Powder Diffraction File – PDF for PC – ICDD). All of these in the XRD Laboratory at the University of Brasilia

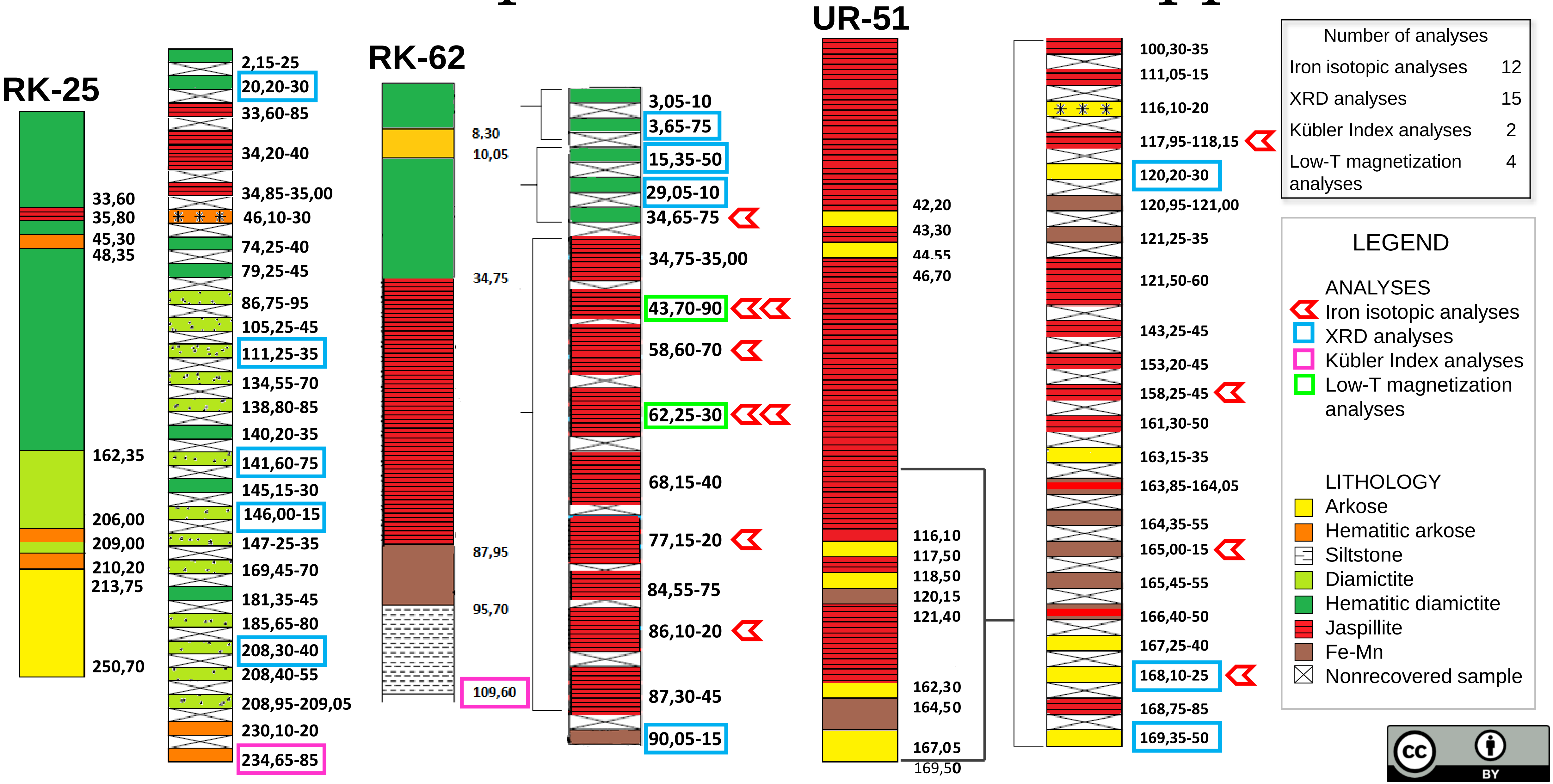
KÜBLER INDEX DETERMINATION

The Kübler Index (KI) is a measure of the full weight at high medium (FWHM), presented in Δº2Ɵ CuKα of d(00l) around 10Å of illite. Through this index it is possible to indicate the diagenetic stage in which the rock was submitted to. To do so, clay fractions were analyzed at reduced velocity of 0,5º/min ranging from 7 to 12 º2Ɵ. Afterwards, we performed a decomposition of the ~10Å peak using the software DecompXR, selecting the diagenetic contribution to finally mesure the KI.

MAGNETIC ANALYSES

In order to attempt to recognize the origin of iron oxides, low-temperature magnetization measurements were carried out, in field cooled (FC) e zero field cooled (ZFC), using a Magnetic Property Measurement System XL (Quantum Design) at the Physics Instituto of the University of Brasilia (coordinated by Dr. José Antonio Huamaní Coaquira).

Drillcores samples and methods applied



Number of analyses	
Iron isotopic analyses	12
XRD analyses	15
Kübler Index analyses	2
Low-T magnetization analyses	4

Iron isotopic analyses

This research:

- Number of analyses= 12;
- Range of $\delta^{57}Fe$ values= -2,836 a 0,094;
- Mean of $\delta^{57}Fe$ values = -1,548;

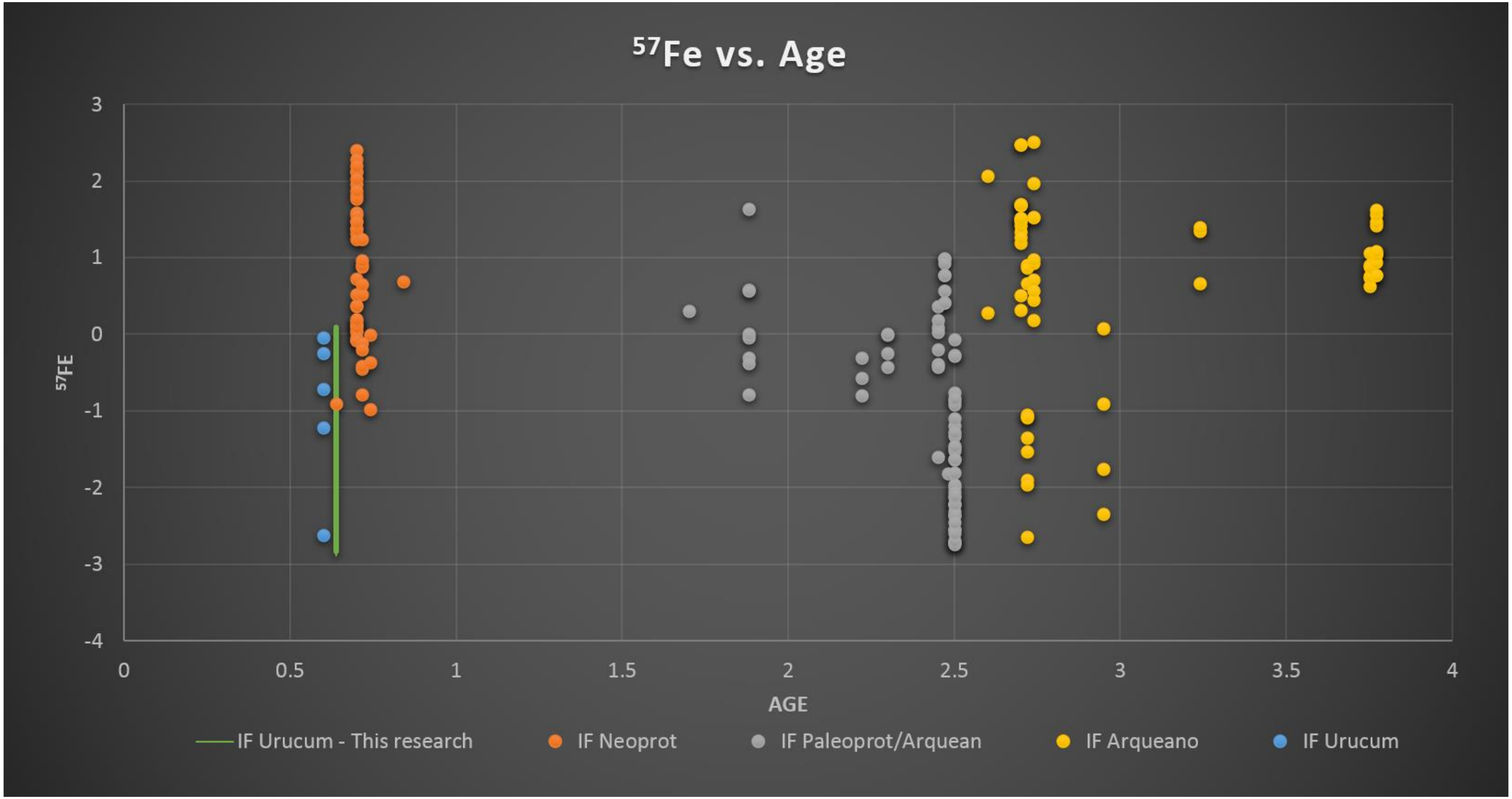
The table aside presents the bulk iron isotopic compilation from iron formations (IF) of different localities through the Precambrian, highlighting the Archean (4.0 – 2.5Ga), the Paleoproterozoic (2.5 – 1.0Ga) and the Neoproterozoic (1.0 – 0.541Ga). A forth classification is the studied area, URUCUM DISTRICT.

These four classes display **n** number of $\delta^{57}Fe$ values, taken in the **references** mentioned and the iron isotopic values present the following **mean**.

Table of descriptive statistics

	n	REFERENCES	MEAN
NEOPROTEROZOIC IRON FORMATION	48	Planavsky et al. 2012; Zhu et al. 2019; Halverson et al. 2011.	0,753
PALEOPROTEROZOIC IRON FORMATION	69	Planavsky et al. 2012; Rouxel et al. 2005; Tsikos et al. 2010.	-0,899
ARCHAEAN IRON FORMATION	63	Planavsky et al. 2012; Rouxel et al. 2005; Dauphas et al. 2007; Czaja et al. 2013.	0,692
URUCUM DISTRICT IRON FORMATION	17	This research; Angerer et al 2016.	-1,377

Statistic analyses



Statistic analyses

TESTING FOR ANOMALY: URUCUM DISTRICT IF and NEOPROTEROZOIC IF

	GOAL	α	ʋ1	ʋ2	Fc	F	Result
F TEST	Describe the probability of obtaining specific ratio between <u>variances</u> of samples of the same population	5%	16	47	1,90	1,109	F<Fcritical There are no reasons to confirm that these samples are from two populations with distinct variances.

NON-CONCLUSIVE

	GOAL	α	ʋ=n1+n2-2	tc	t	Result
T TEST **(TWO-SAMPLES)**	Describe the probability of obtaining specific ratio between <u>means</u> of samples of the same population	10%	63	± 1,64	-1,7087	t<tcritical <u>The two samples are from two populations with distinct means.</u> **CONCLUSIVE**

Statistic analyses

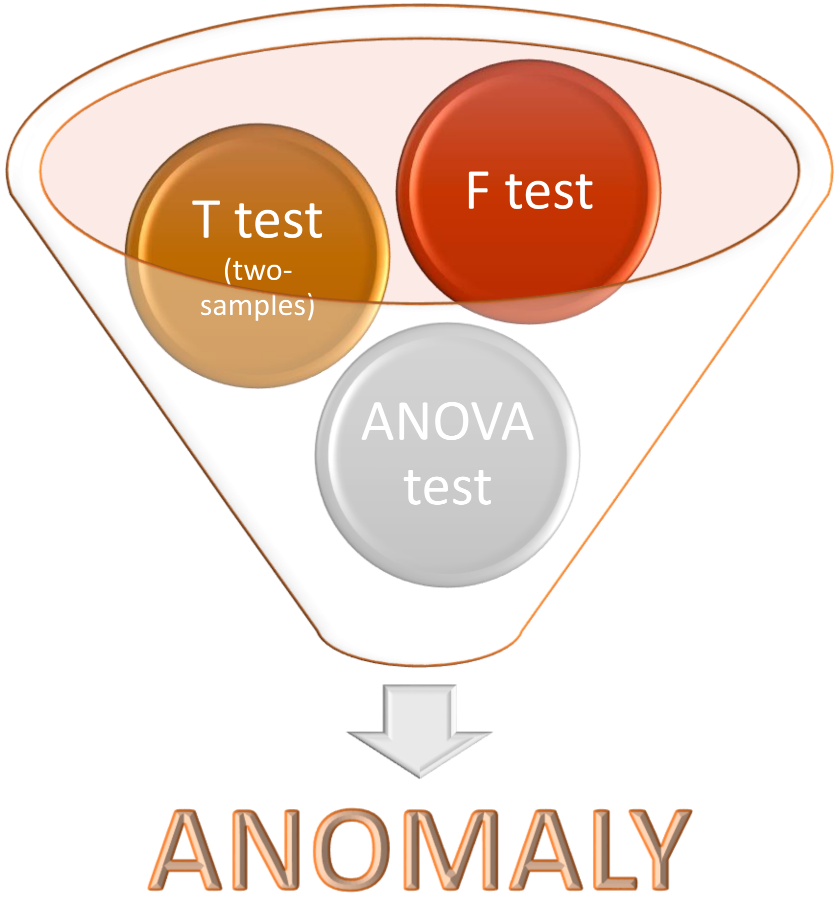
TESTING FOR ANOMALY: URUCUM DISTRICT IF and NEOPROTEROZOIC IF

	GOAL	α	υ1	υ2	Fc	F	Result
ANOVA TEST	Analysis of variance (ANOVA) is a collection of statistical models and their associated estimation procedures used to analyse the differences among group means in a sample.	5%	1	63	4,0	28,623	F>Fcritical There are reasons to confirm that these samples are from two populations with distinct variances. **CONCLUSIVE**

Statistic analyses

RESULT

The values of $\delta^{57}Fe$ of the Iron Formation from the Urucum District are **STATISTICALLY AMALOUS**, when compared to the ones from the compilation of bulk $\delta^{57}Fe$ values of Neoproterozoic iron formations.



Diagenetic evaluation

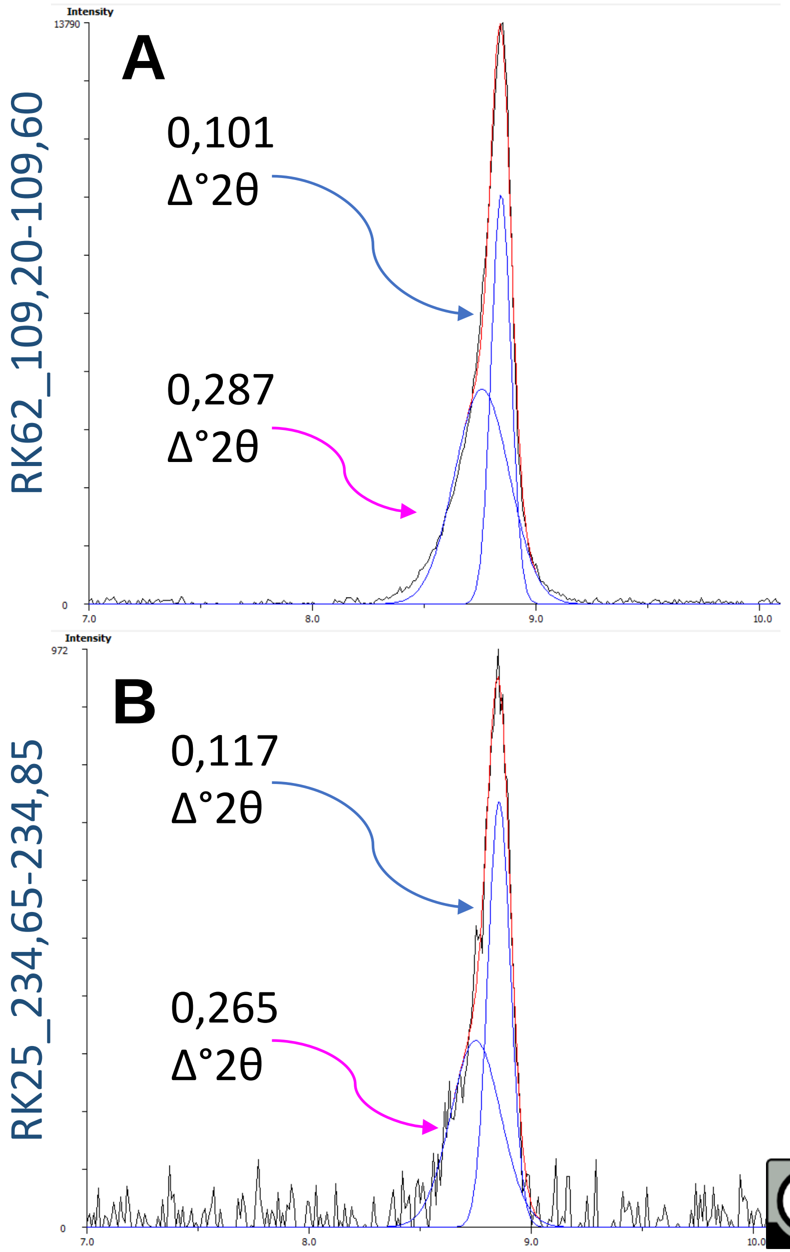
XRD and Kübler Index analyses.

Focused in the matrix of diamictites and in siliciclastic facies (arkoases, sandstones and siltstones).

The presence of expansive clay minerals indicate a diagenesis to anchizone stage.

The Kübler Indexes, determinated by diagenetic illites, also point into **anchizone stage**, according to Kübler (1964) as well as Kisch (1987), Merriman & Frey (1999), Merriman & Peacor (1999), Warr & Mählmann (2015) and many others.

SAMPLE	CURVES	N			
		POSITION	INTENSITY	FWHM	%
RK62_109,20-60 **(figure A)**	#1	8,836	6671	0,101	99,56%
	#2	8,75	3412,3	0,287	
RK25_234,65-85 **(figure B)**	#1	8,847	488,8	0,117	95,61%
	#2	8,742	209,9	0,265	



Magnetic Analyses

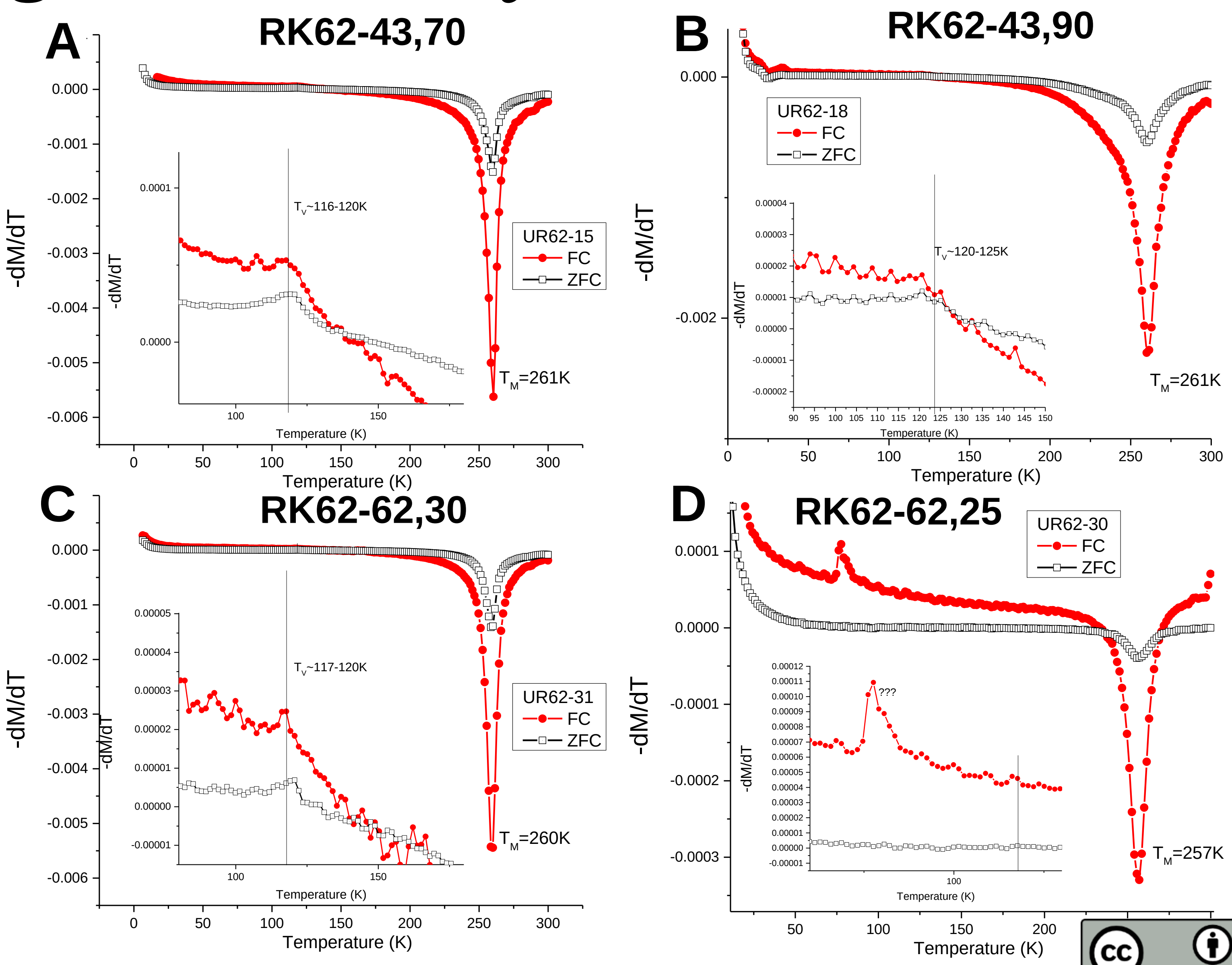
These measurements were performed in order to identify the transition phases between different magnetic fractions, in particular the Verwey (~120 K) and the Morin (~260 K) transitions for stoichiometric magnetite and hematite, respectively (in figs. **A-D**).

These magnetic measurements were performed in field cooled (FC) e zero field cooled (ZFC), presented by the red and black curves, respectively.

These four samples were selected by their intense fractionated $\delta^{57}Fe$ values.

It’s possible to observe both Verwey (~120 K) and Morin (~260 K) transitions in three samples: RK62-62,30; RK62-43,70 and RK62-43,90 (figs. **A-C**). In RK62-62,25, only the Morin transition is clear (fig. **D**).

That can be explained due to the nature of the samples. Samples A-C are classified as iron formations, and sample D is interpreted as a chert.

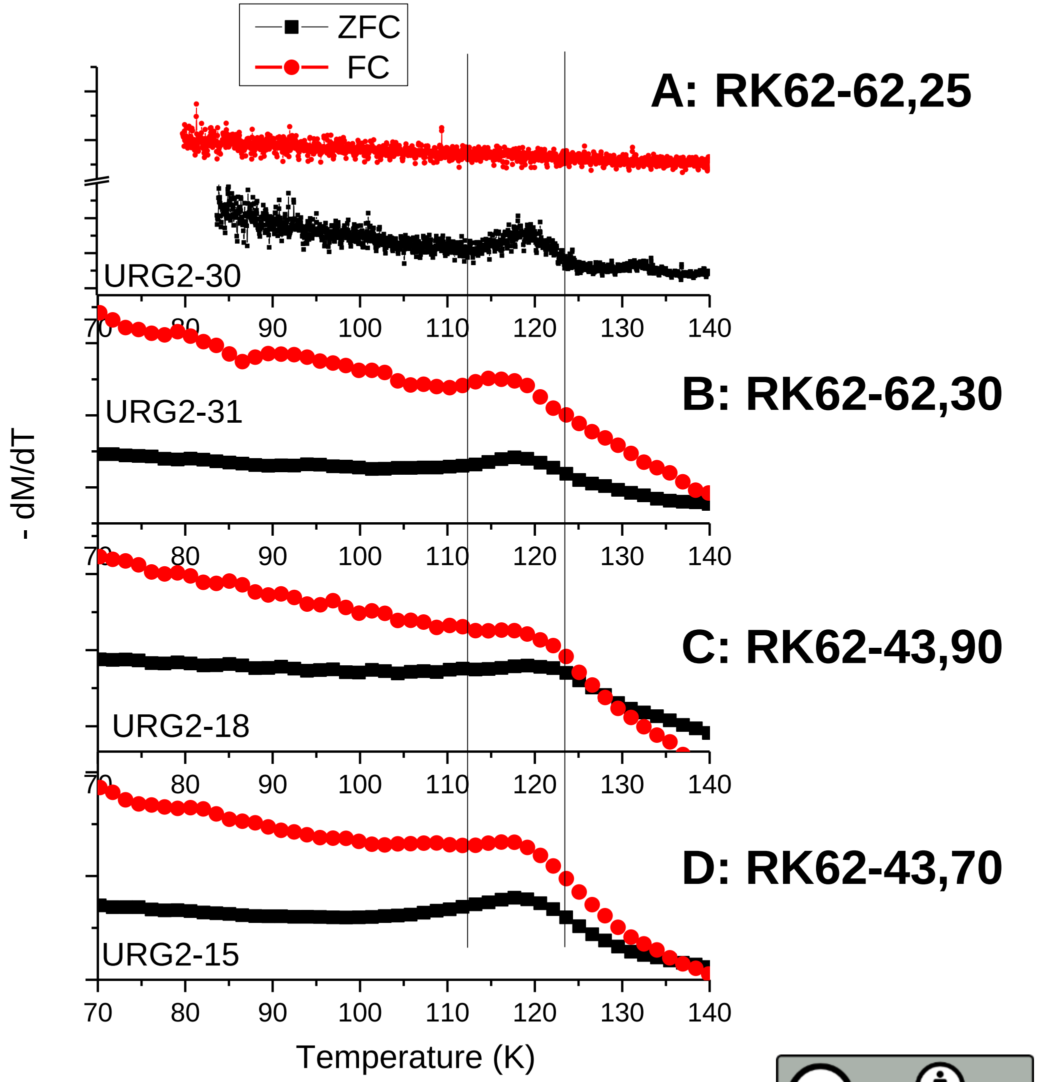


Magnetic Analyses

Low temperature data (FC/ZFC curves), other than identify the transition phases between different magnetic fractions, can highlight a biogenicity of magnetites, by presenting two distinct peaks at 100 and 120 K (Chang et al. 2016; Caleffo et al. 2019).

As we observe this interval closely (fig. A-D), sample **A** (chert) is still unclear regarding the presence of magnetite and samples **B**, **C** and **D** show clearly the Verwey transition around 120K.

It's important to emphasize that sample B: RK62-62,30, points towards a double Verwey transition but it's not well defined. This can be explained due to the noisy data and low concentration of magnetite in these samples when compared to the hematite phase.



Discussion

The iron isotopic signatures of Urucum District's IF are STATISTICALLY ANOMALOUS when compared to the bulk iron isotopic compilation, pointing towards an intense fractionation process.

The question to be answered here is: **Why are the δ^{57}Fe signatures of the Urucum District's IF fractionated?**

We investigate the possible processes for iron isotopes fractionation, they are:

- WEATHERING: not applied, due to the drillcore's nature of the analysed samples;
- DIAGENESIS/METAMORPHISM: According to XRD interpretations and Kübler index determination, the samples were subjected to an anchizone temperature/pressure at maximum, not relevant for iron isotopic fractioning processes;
- METABOLIC ACTIVITY OF PLANKTONIC BACTERIA: we attempt to recognize biogenic magnetite with low-temperature magnetization measurements, but it is still inconclusive. Bacteria enrolment in the (post-)deposition process can be related to the iron isotopic fractionation.

The search for the answer continues...

In the next phases of this research, we intent to search for more conclusive results for the origin of the magnetite, if it is biogenic or detritic.

In order to do so, we plan to use Electric Transmission Microprobe (ETM), Magnetic Resonance, Scanning Magnetic Microscopy (SMM) and other magnetic measurements.

We also intent to concentrate the magnetite phase and repeat the low-temperature magnetization measurements, to reduce data noise.

Acknowledgements

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The authors specially thank our newest collaborator, Dr. José Antonio Huamaní Coaquira (Phisics Institute of the University of Brasília), who is been supporting our work specifically with the low temperature magnetization analyses.

This is an ongoing research that will soon be submitted to publication.

We are open to suggestions and to clear up any doubts.

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