Supplementary Material B

Complete Lu-Hf procedures

1. Lu-Hf procedures

The Lu-Hf isotopic system is one of the most innovative and powerful tools in zircon geochronology [e.g. 1-9]. The Lu-Hf technique is applied to zircon grains because this mineral has high Hf concentration, due to its substitution by Zr, and to preserve the initial ratios of Hf. The blocking temperature of the Hf in the zircon is about 200 °C higher than the Pb (approximately 1,100 °C), indicating that the Hf isotopic system is closed during almost all thermal events, such as high-grade metamorphism, maintaining the isotopic ratios present in the zircon crystallization [10 – 12]. The models of Hf isotopic evolution have been proposed based on the hypothesis of the use of the Hafnium as a marker of the geochemical differentiation between mantle and crust [1, 8, 13, 14]. In this sense, interpretations of ε_{Hf} values are similar to that of ε_{Nd} values being able to indicate mantle-derived rocks or rocks originating from crustal magmas (if the values are positive or negative, respectively). It has been widely used for understanding crustal evolution and mantle/crust differentiation.

The acquisition of Lu-Hf data is carried out following a sequence that begins with the choice of the grain to be analyzed and the place where the crater will be made, usually in the place where the U-Pb age was performed, however with a diameter of 40-50μ. For this, the CL images and the image provided by the equipment's camera are counted on, then the laser spot is positioned, and the beam is manually activated, initiating the ablation process. Material ablated by laser was carried using Ar and He and it takes a few seconds (3-10) for the signal to stabilize. In sequence, data acquisition is initiated in 40 cycles (1.045 seconds each cycle).

The collectors were positioned as follows (Table 1): in the central collector the mass ^{176}Hf, in the collectors H1 mass ^{177}Hf, H2 mass ^{178}Hf and H3 mass ^{179}Hf. In the collectors L1 the mass ^{175}Lu, L2 the mass ^{174}Hf, L3 the mass ^{173}Yb and in L4 the mass ^{171}Yb. The isobaric corrections were installed in the mass spectrometer software, so that the interferences ^{176}Lu and ^{176}Yb have their abundances obtained through the measurements of the masses ^{173}Yb and ^{175}Lu. Thus, the correction factors of 0.795015 and 0.026580, respectively, were used. The correction of the isotopic fractionation of the mass spectrometer is performed from the constant ratios ^{179}Hf / ^{177}Hf (true value 0.7325) and ^{171}Yb / ^{173}Yb (true value of 1.123456) reported in the literature [15 – 17].

Table 1 - Configuration of the Faraday collectors used for the Lu and Hf analyzes.

Faraday collectors	**H3**	**H2**	**H1**	**C**	**L1**	**L2**	**L3**	**L4**
Isotopes	^{179}Hf	^{178}Hf	^{177}Hf	^{176}Hf	^{175}Lu	^{174}Hf	^{173}Yb	^{171}Yb
Interferers				^{176}(Yb+Lu)		^{174}Yb		

A calibration procedure of Faraday detectors (presented in Table 2) was then performed using the reference material solution (JMC475) through plasma settings and gas (Ar) flows for signal optimization [4]. Isotopic data were obtained using the static mode through 50 cycles of 1.054 seconds acquirement time with a gas inlet flow (Ar) of 15 L / min, auxiliary flow (Ar) 0.8 L / min. in MC-ICP-MS. The laser was connected and suitable He (two input streams with volumes of 0.800 l / m and 0.220 l / m, totaling 1.020 l / m). Repetition of the laser was at 10 Hz, with 4-7 J / cm2 (35-60%) output power and 40 µm crater size.

Table 2. Operating conditions of LA-ICP-MC-MS in the Lu-Hf method.

ICP-MC-MS-NEPTUNE PLUS (Thermo Scientific)	
RF Energy	1200W
Gas flow:	Ar Cool: 15 L/min
	Ar Aux: 0.73 L/min
	Ar carrier: 0.85 L/Min
Analysis Mode:	Static
Detectors:	Faradays
Aquisition time:	1.045 s
Laser ablation - Photon Machines In. 193 mm	
Crater diameter:	40 - 50 µm
Laser pulse energy:	4 - 7 J/cm^2
Frequence:	10 Hz
Abration time:	50 s
Fgas flow (He):	0.80 L/min
Gas flow (He):	0.22 L/min

2. Lu-Hf Calibrations

The values of the abundances of the Hf, Lu and Yb isotopes were shown to be effective according to three reference material used (GJ-1, Mud Tank and 91500). In the calibration of the Lu-Hf method using laser ablation, the ^{176}Hf/^{177}Hf ratios of the GJ-1 reference material were initially analyzed. The GJ-1 (Figure 1) is used in large scale by geochronology laboratories being reference material for U-Pb and Lu-Hf isotopic analysis. The isotopic ratios ^{176}Lu/^{177}Hf and

$^{176}Hf/^{177}Hf$ of this reference material are reported in the literature with values of 0.00025 and 0.282005, respectively [17 – 19]. In the calibration of the method using laser, the $^{176}Hf/^{177}Hf$ ratios of the GJ-1 like the reference material published were obtained. Its mean value is 0.282016, which is almost identical to the recommended value in the literature.

A second reference material used during the analysis is comprised of the Mud Tank (Figure 1), a natural zircon collected a carbonatite that outcrops in Strangways, east of Alice Springs (Australia). The carbonatite has an age of 732 Ma with large amounts of zircon and apatite crystals up to ten centimeters. The obtained isotopic ratios $^{176}Lu/^{177}Hf$ and $^{176}Hf/^{177}Hf$ indicate values of 0.000042 and 0.2882507 and are equivalent to those described in the literature for the Mud Tank reference material [18]. The 91500 (Figure 1) reference material is also used and was part of the Harvard Museum collection and was carefully prepared as a reference material after a preliminary characterization, including Lu-Hf isotopic analyzes. Zircon 91500 has been widely adopted by many laboratories as reference material for Lu-Hf analyzes. The isotopic ratios values of 0.000311 ($^{176}Lu/^{177}Hf$) and 0.2882305 ($^{176}Hf/^{177}Hf$) were determined and are consistent with the reported true value [17, 19].

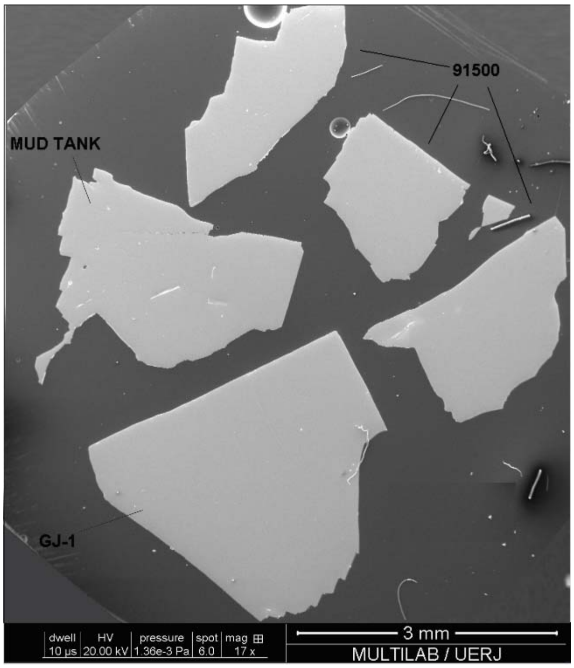

Figure 1 - SEM images of the reference materials used for calibration of the Lu-Hf method in LA-ICP-MS in the MultiLab laboratory (UERJ).

1.4 Data calculations and Yb isobaric interference correction

The data are recorded by computers that are coupled to the mass spectrometer and then transferred to another computer for processing in Excel where GJ-1 values obtained are compared with true values in order to calculate T_{DM} and ε_{Hf} values. Finally, the Excel spreadsheet is used to make the Hf isotopic evolution diagrams [17, 19]. The procedure works in order to correct the average of the final blank and for reference materials (detailed procedures may be found in [20]). T_{DM} ages and ε_{Hf} were calculated assuming an average crustal $^{176}Lu/^{177}Hf$ value of 0.01250 [2, 13, 21], using an offline Excel spreadsheet [22]. In all the tables and figures, the initial ε_{Hf} was calculated using present-day CHUR values of $^{176}Hf/^{177}Hf$ = 0.282785 and $^{176}Lu/^{177}Hf$ = 0.0336 [23]. For diagrams of the crustal and depleted mantle evolution curves the present-day values for $^{176}Hf/^{177}Hf$ in the depleted mantle and Archean crust are 0.283214 and 0.280554, respectively, and corresponding values for $^{176}Lu/^{177}Hf$ are 0.0399 and 0.0024 [14, 24].

The GJ-01, 91500 and Mud Tank reference materials were analyzed in order to determine the Lu, Hf and Yb isobaric interference. The objective of the analyzes was to identify the abundances of ^{176}Lu and ^{176}Yb and thus to identify the efficiency of isobaric interference correction. For this purpose, in each reference material (GJ-01, 91500 and Mud Tank) the abundances of ^{176}Hf, ^{177}Hf, ^{178}Hf, ^{179}Hf, ^{175}Lu, ^{174}Hf, ^{173}Yb and ^{171}Yb were measured. From the values of ^{173}Yb and ^{175}Lu the abundances of ^{176}Lu and ^{176}Yb were calculated and subtracted from the values of ^{176}Hf, thus obtaining the abundance of this corrected isotope of its isobaric interferences. The correction of the values of ^{176}Lu is performed through the measures of abundances of masses ^{173}Yb and ^{175}Lu and the correction factors of 0.795015 and 0.026580 respectively. A zircon pattern with the least possible amount of Yb results in the application of lower correction factors and may result in more accurate results.

The measured values of mass 176 (Lu + Hf + Yb) corresponds to the highest intensity value (data in cps - counts per second). The values of ^{176}Lu, ^{176}Hf and ^{176}Yb were plotted individually, so it is possible to evaluate the absolute amount for each of these isotopes. When comparing the sum of the three masses (^{176}Lu, ^{176}Hf and ^{176}Yb), we can see the GJ-01 zircon and 91500 have significant values of ^{176}Lu and ^{176}Yb, but Mud Tank zircon shows values of ^{176}Lu and ^{176}Yb closer to zero, which facilitates the correction of the isobaric interferences. Therefore, it is possible to characterize the Mud Tank as the zircon with less abundance of Yb, and thus to indicate this reference material as the best among the three when evaluated by the need for isobaric interference correction of ^{176}Lu and ^{176}Yb over ^{176}Hf.

The values of the abundances of the Hf, Lu and Yb isotopes were shown to be effective, and the three-reference material used during the analyzes reproduced the values with error margins comparable to the literature data, with intensity of signals enough to obtain stable and statistically reliable results. Once the calibrations of reference material solutions and zircon reference material demonstrated the efficiency of Yb interference on Lu, the Lu-Hf method was used for unknown samples.

References

1. Amelin, Y., Lee, D.-C., Halliday, A. N. and Pidgeon, R. T. Nature of the Earth's earliest crust from hafnium isotopes in single detrital zircons. *Nature* **1999**, *399*, 252–5.
2. Griffin, W.L., Pearson, N.J., Belousova, E., Jackson, S.E., O'reilly, S.Y., Van Achterberg, E., Shee, S.R. The Hf isotope composition of cratonic mantle: LAM-MC-ICPMS analysis of zircon megacrysts in kimberlites. *Geochim Cosmochim Ac* **2000**,*64*, 133–147.
3. Griffin, W.L., Wang, X., Jackson, S.E., Pearson, S.E., O'Reilly, S.Y., Xu, X.S., Zhou, X.M. Zircon chemistry and magma genesis, SE China: in-situ analysis of Hf isotopes, Tonglu and Pingtan Igneous Complexes. *Lithos* **2002,** *61*, 237–269.
4. Woodhead, J., Hergt, J., Shelley, M., Eggins, S., Kemp, R., . Zircon Hf-isotope analysis with an excimer laser, depth profiling, ablation of complex geometries and concomitant age estimation. *Chem. Geol.* **2004**, *209*, 121–135.
5. Belousova E, Griffin W, O'Reilly S.Y. Zircon crystal morphology, trace element signatures and Hf isotope composition as a tool for petrogenetic modelling: examples from Eastern Australian granitoids. *J Petrol.* **2005**, *47*, 329–53.
6. Gerdes, A., Zeh, A. Zircon formation versus zircon alteration – New insights from combined U-Pb and Lu-Hf in-situ LA-ICP-MS analyses, and consequences for the interpretation of Archean zircon from the Central Zone of the Limpopo Belt. *Chem. Geol.* **2009,** *261*, 230–243.
7. Gerdes, A., Zeh, A. Combined U-Pb and Hf isotope LA-(MC)-ICP-MS analyses of detrital zircons: comparison with SHRIMP and new constraints for the provenance and age of an Armorican metasediment in Central Germany. *Earth Planet Sc Lett* **2006,** *249*, 47–61.
8. Hawkesworth, C.J. e Kemp, A.I.S (2006): Using hafnium and oxygen isotopes in zircons to unravel the record of crustal evolution. *Chem. Geol.* **2006,** *226*, 144–162
9. Zeh, A., Gerdes A., Klemd R., Barton Jr Jm. . Archaean to Proterozoic Crustal Evolution in the Central Zone of the Limpopo Belt (South Africa-Botswana): Constraints from Combined U-Pb and Lu-Hf Isotope Analyses of Zircon. *J Petrol.* **2007**, 48, 1605–1639.
10. Duchene, S., Blichert-Toft, J., Luais, B., Telouk, P. Albarede, F., . The Lu–Hf dating of garnets and the ages of the Alpine high-pressure metamorphism. *Nature* **1997**, *387*, 586–9.
11. Choi, S.H., Mukasa, S.B., Andronikov, A., Osanai, Y., Harley, S., Kelly, N. Lu–Hf systematics of the ultra-high temperature Napier Metamorphic Complex in Antarctica: Evidence for the early Archean differentiation of Earth's mantle. *Earth Planet. Sci. Lett.* **2006,** *246*, 305–316.
12. Schmidt, A., Weyer, S., Mezger, S., Scherer, E., Xiao, Y., Hoefs, J., Brey, J. Rapid eclogitisation of the Dabie–Sulu UHP terrane: Constraints from Lu–Hf garnet geochronology. *Earth Planet. Sci. Lett.* **2008**, *273*,203–213.

13. Patchett, P.J., Kouvo, O., Hedge, C.E. and Tatsumoto, M. Evolution of continental crust and mantle heterogeneity: evidence from Hf isotopes. *Contrib. Miner. Petrol.* **1981**, *78*, 279–297.
14. Vervoort, JD., Blichert-Toft, J. Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. Geochimica et Cosmochimica Acta, **1999**, *63*, 533–556. https://doi.org/10.1016/S0016-7037(98)00274-9.
15. Patchett, P. J. And Tatsumoto,M. Hafnium isotope variations in oceanic basalts. *Geophys Res Lett* **1980**, *7*, 10771080.
16. Patchett P. J. and Tatsumoto M. Lu/Hf in chondrites and definition of a chondritic hafnium growth curve. *Lunar Planet. Sci.* **1981**, *12*, 822.
17. Morel, M.L.A., Nebel, O., Nebel-Jacobsen, Y.J., Miller, J.S., Vroon, P.Z. Hafnium isotope characterization of the GJ-1 zircon reference material by solution and laser-ablation MC-ICPMS. *Chem. Geol.* **2008**, *255*, 231–235.
18. Woodhead, J.D., Hergt, J.M. A preliminary appraisal of seven natural zircon reference materials for in situ Hf isotope determination. Geostand. Geoanalyt. Res. **2005**, *29*, 183–195.
19. Elhlou, S., Belousova, E., Griffin, W.L., Pearson, N.J. and O'reilly, S.Y. Trace element and isotopic composition of GJ-red zircon reference material by laser ablation. *Geochim. et Cosmochim. Acta* **2006**, *70*, 158–158.
20. Alves, M.I., Almeida, B.S., Cardoso, L.M.C., Santos, A.C., Appi, C., Bertotti, A.L., Chemale, F., Tavares Jr, A.D., Martons, M.V.A., Geraldes, M.C. Isotopic Composition of Lu, Hf and Yb in GJ-1, 91500 and Mud Tank reference materials measured by LA-ICP-MS: Application of the Lu-Hf geochronology in zircon. *J. Sediment. Environ.* **2019**, *4*, 220–248.
21. Chauvel, C.,Garçon, M., Bureau,S., Besnault, A., JahnB.-M. and Ding Z. L. Constraints from loess on the Hf-Nd isotopic composition of the upper continental crust, *Earth Planet. Sci. Lett.* **2014,** *388*, 48–58.
22. Bertotti, A. L.; Chemale Jr., Farid; Kawashita, Koji. Lu-Hf em Zircão por LA-ICP-MS: Aplicação em Gabro do Ofiolito de Aburrá, Colômbia. Pesquisas em Geociências **2013**, *40*, 117–127.
23. Bouvier A., Vervoort J.D. and Patchett P.J. () The Lu–Hf and Sm–Nd isotopic composition of CHUR: constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. *Earth Planet. Sci. Lett.* **2008,** *273*, 48–57.
24. Patchett, P.J., Tatsumoto, M. Hafnium isotope variations in oceanic basalts. *Geophys. Res Lett* **1980**, *7*, 1077–1080.