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# Sequential leaching of silicified Archaean carbonates: A Rb-Sr, Sm-Nd and Pb-Pb isotopic contribution to their tectonic-thermal history (Kaapvaal Craton, South Africa)

Theofilos Toulkeridis, Norbert Clauer, I. Tonguç Uysal, Alfred Kröner

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1           **Sequential leaching of silicified Archaean carbonates: a Rb-Sr, Sm-Nd**  
2                           **and Pb-Pb isotopic contribution to their tectonic-thermal**  
3                           **history (Kaapvaal Craton, South Africa)**

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6           Theofilos Toulkeridis<sup>1</sup>, Norbert Clauer<sup>2</sup>, I. Tonguç Uysal<sup>3</sup> and Alfred Kröner<sup>4</sup>

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9           <sup>1</sup> Universidad de las Fuerzas Armadas ESPE, Sangolquí, Ecuador

10          <sup>2</sup> Institut des Sciences de la Terre et de l'Environnement de Strasbourg, Université de  
11          Strasbourg, (UdS/CNRS), 67084 Strasbourg, France

12          <sup>3</sup> Department of Geology, Faculty of Engineering, University of Istanbul-Cerrahpasa,  
13          Istanbul, Turkey

14          <sup>4</sup>Institut für Geowissenschaften, Mainz University, 55099 Mainz, Germany

15  
16  
17          **Abstract**

18                 Sequential leaching was completed by successive interactions of ultra-pure H<sub>2</sub>O, HAc,  
19                 HCl and HNO<sub>3</sub> with silicified/carbonated Archaean whole rocks from Barberton Greenstone  
20                 belt of South Africa. The purpose of this experiment was an identification of the minerals  
21                 interacting with each reagent and, therefore, a detailed succession of isotopically dated  
22                 tectonic-thermal episodes recorded in these minerals. The contents of the major, trace and  
23                 rare-earth elemental, together with the Sr, Nd and Pb isotopic compositions of untreated,  
24                 leachate and residue triplets allowed identification and analysis of various types of carbonates  
25                 and sulfates mixed with insoluble silicates. The samples yield two overall geological age  
26                 milestones at  $2.9 \pm 0.1$  and  $2.1 \pm 0.1$  Ga, as well as varied age values, some with large  
27                 uncertainties. A further event at about  $1.6 \pm 0.1$  Ga is suggested probably in relation with the  
28                 emplacement of the Bushveld complex or of further intrusive complexes of the Kaapvaal  
29                 Craton.

30                 While the basics of the different used isotopic systems can be considered to be similar,  
31                 the Rb-Sr method appears to be the best suited to detail the studied rocks, especially their  
32                 sensitive soluble minerals. The Sm-Nd method is less flexible because of its inherent need of  
33                 widely ranging Sm/Nd ratios that depend on the mineral assemblage. In the case of the Rb-Sr

34 ages well constrained by isochron arrays, more similar ages were obtained by tentatively  
35 called isotrends that consist in data points slightly scattered along the arrays giving higher  
36 uncertainties, especially with the Sm-Nd method. The fact that these isotrends gave similar  
37 ages in addition to those of the isochrons comforts the historic evolution of the studied  
38 material.

39 These scatters most probably correspond to slight changes in the chemical  
40 characteristics of minerals leached by the successive reagents, but analytical uncertainties  
41 cannot be completely excluded, especially in the case of the HNO<sub>3</sub> leaching step. Finally, the  
42 Pb-Pb method appears to be of a more limited application, possibly because of possible metal  
43 contamination of the host rocks, either during their evolution in a region characterized by  
44 metal-rich concentrations or more recently during discrete surficial to sub-surficial  
45 alteration/weathering processes. In terms of leaching efficiency, that with H<sub>2</sub>O removed  
46 expectedly the lowest amounts of soluble components followed by HNO<sub>3</sub>, the two efficient  
47 removers being dilute HAc and HCl. In turn, the obtained geochronological ages consolidate  
48 previously published ages that concentrate on post-depositional tectonic-thermal events within  
49 the Kaapvaal Craton during about 1.0 Ga. However, they also suggest some reconsideration  
50 for other ages of the literature.

51

52

53 **Keywords:** sequential leaching procedure; Rb-Sr, Sm-Nd and Pb-Pb isotope systematics;  
54 isochron vs. isotrend arrays; REE distribution patterns; post-depositional thermal events;  
55 Barberton Greenstone Belt

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57

## 58 **Introduction**

59 Carbonates represent a minor lithofacies of early Precambrian greenstone belts, but  
60 they are of interest as they are able to record tectonic-thermal steps, as well as changes of the  
61 atmospheric and oceanic environments during deposition and further recrystallization  
62 episodes (e.g., Schidlowski et al., 1975; Veizer et al., 1989; Shields and Veizer, 2002).  
63 Because of their sensitivity to multiple alteration processes, these rocks may also provide  
64 useful information about the successive post-depositional metamorphic, diagenetic and  
65 hydrothermal activities to which they were potentially subjected (e.g., Wang et al., 2018). For  
66 instance, Jahn and Cuvellier (1994) published a summary of the isotopic behavior of

67 carbonated Archaean rocks with useful identification aspects of successive depositional and  
68 diagenetic/metamorphic events during their evolution.

69 Historic information was also obtained by removing the soluble components of whole  
70 rocks in geochronological studies of Archaean carbonates with various reagents and by dating  
71 the obtained aliquots separately. In fact, since the initial Pb-Pb dating of carbonate whole  
72 rocks by Doe (1970) and later by Moorbath et al. (1987), many investigations were published  
73 to substantiate and enlarge the application of leaching techniques combined with various  
74 isotopic methods. Such applications to various sedimentary to meta-sedimentary carbonates,  
75 especially of old to very old ones that were lacking fossils of stratigraphic use, were of  
76 determining use for evaluating the potentials of new dating methods (e.g., Schwarcz and  
77 Latham, 1989; Jahn et al., 1990; Bischoff and Fitzpatrick, 1991; Luo and Ku, 1991; Erel et al.,  
78 1997; Babinski et al., 1999; Fölling et al., 2000; Melezhik et al., 2001; Bolhar et al., 2002;  
79 Kaurova et al., 2010; Bellefroid et al., 2018). These references reveal the interest of these  
80 rocks and methods for many geochronologists during decades. However, as often, such  
81 published studies did not always release unequivocal stratigraphic “ages” for various reasons,  
82 one being due to specific methodological aspects depending often on the characteristics of  
83 each isotopic method, as well as of the minerals on which they were applied. In order to  
84 increase potentially the information about the meaning of such results, especially on whole  
85 rocks that may host minerals of successive origins and/or differential evolutions, a sequential  
86 leaching procedure has been used here to evaluate further the soluble components of a few  
87 carbonates from early Archaean Barberton Greenstone Belt of South Africa. Initially, the  
88 purpose was the diversification of successively dissolved constituents by using reagents with  
89 a progressive impact on the carbonate-type minerals of the rocks. The goal was an estimation  
90 of what meant the Rb-Sr, Sm-Nd and Pb-Pb data of systems known for their variable  
91 signatures relative to successive tectonic-thermal events. In turn, a complementary goal of the  
92 study was an integrated understanding of the global evolution of these ancient rocks by a  
93 combination of various isotopic age data.

94

## 95 **The geological and geochronological context**

96 Located near the southeastern edge of the Kaapvaal craton in South Africa, the  
97 Barberton Greenstone Belt consists of deformed and variably metamorphosed sedimentary  
98 and volcanic rocks of the Swaziland Supergroup (e.g., South African Committee for  
99 Stratigraphy, 1980; Fig. 1). These supra-crustal units are in structural or intrusive contact with  
100 surrounding coeval or younger granitoid plutons (Anhaeusser, 1973; Anhaeusser and Robb,

101 1981). The lower 8 to 10 km thick succession of this Swaziland Supergroup belongs to the  
102 ~3.5 to ~3.3 Ga old Onverwacht Group (Kröner and Todt, 1988; Armstrong et al., 1990;  
103 Lopez-Martinez et al., 1992), consisting mainly of mafic and ultramafic volcanic rocks with  
104 minor sedimentary and felsic layers (e.g., Viljoen and Viljoen, 1969; Lowe and Byerly,  
105 2007). It is overlain, apparently conformably, by a dominantly sedimentary sequence that  
106 includes the Fig Tree and Moodies Groups.

107 On top of the Onverwacht Group, the predominantly sedimentary Fig Tree Group of a  
108 stratigraphic age of about 3.28 to 3.24 Ga and even to 3.22 Ga in some places (Kröner et al.,  
109 1991; Kamo and Davies, 1993) and the Moodies Group consist mostly of a 1 to 3 km thick  
110 succession of graywackes, shales, cherts, as well as of dacitic and felsic volcanics (Heubeck  
111 and Lowe, 1994; Lowe and Nocita, 1999; Eriksson and Simpson, 2000; Heubeck et al., 2013;  
112 Wabo et al., 2018). The youngest carbonate unit of this Fig Tree sequence that includes the  
113 samples studied here belongs to the Mapepe Formation (Lowe and Nocita, 1999; Drabon et  
114 al., 2019). Although virtually all Barberton rocks were affected by a low-grade metasomatic  
115 alteration that involved silicification, carbonatization and widespread crystallization of  
116 secondary sericite and chlorite, they preserved their primary structures and textures (e.g.,  
117 Lowe, 1991). These reactions, especially the wide crystallization of sericite known to carry  
118 Rb are expected to impact at least the Rb-Sr system that might be the most affected by the  
119 observed metasomatic alterations.

120 All units of the Greenstone belt were topics of numerous geochronological (e.g.,  
121 Allsopp et al., 1973; Barton et al., 1983; Armstrong et al., 1990; de Vries et al., 2006; Zeh et  
122 al., 2011; 2013; Furnes et al., 2013; Decker et al., 2015), structural (De Ronde et al., 1991;  
123 Heubeck and Lowe, 1994; Van Kranendonk et al., 2009; Grosch et al., 2011), metamorphic  
124 (Stevens and Moyen, 2007; Grosch et al., 2012; Cutts et al., 2014) and sedimentologic  
125 investigations (Eriksson et al., 1994; Lowe and Nocita, 1999; Toulkeridis et al., 1999; Westall  
126 et al., 2006; Hessler and Lowe, 2006; Hofmann and Bolhar, 2007; Heubeck, 2009; de Wit et  
127 al., 2011; Heubeck et al., 2013). The published results showed that major thermal events  
128 affected the belt after deposition of the Moodies Group at ~3.1, ~2.7, ~2.4 and ~2.1 Ga (Weis  
129 and Wasserburg, 1987; De Ronde et al., 1991; Poujol et al., 2003; Tice et al., 2004; Hofmann,  
130 2005; Anhaeusser, 2006; Lana et al., 2011; Hofmann et al., 2013; Anhaeusser, 2014;  
131 Toulkeridis et al., 2015). However, it is needed to recall that most of these geochronological  
132 results were based on single applications of classical isotopic methods to whole rocks with  
133 complex histories and that, therefore, they may no longer be considered strictly and  
134 systematically as age milestones. More independent analytical data are certainly welcome to

135 consolidate the milestone ages in rocks that underwent several, sometimes discrete or even  
136 unknown events. Until now, the geochronological issue in isotopic dating of tectonic-thermal  
137 events in Archean rocks was often based on the search of already published “identical ages”  
138 rather than of specific records imprinted on specific types of rocks. A multi-method approach  
139 including three isotopic systems applied to rocks of various compositions due to specific  
140 evolutions was attempted in the herein experiment, tentatively to follow a more mineralogical  
141 than historical approach that includes successive leaching of the same rock with several  
142 impacting reagents.

143         The four Fig Tree carbonated rocks that were sequentially subjected here to such  
144 leaching experiments were previously part of a dating study of untreated whole rocks by the  
145 same isotopic methods (Toulkeridis et al., 1998). They belong, together with two duplicates of  
146 one of the samples, to the Mapepe Formation that is a 40-m thick sequence consisting of  
147 cherts, dolomitic carbonates and terrigenous clastic rocks of the Eastern Barite Valley (Fig.  
148 1). This mostly carbonated rock unit contains also thin beds of jasper and translucent grey  
149 cherts with a barite horizon underneath the carbonates. The lithofacies was deposited on a  
150 well-developed shallow platform in the so-called Barite Syncline (Heinrichs and Reimer,  
151 1977; Lowe and Nocita, 1999; Drabon et al., 2019). The selected FTG1 sample is laminated  
152 and fine-grained, consisting primarily of idiomorphic dolomite and quartz with minor Ba-rich  
153 illite that are all dispersed in a fine-silicified carbonate (Fig. 2). The three other selected  
154 samples (FTG2 to FTG4) are coarser grained and consist mostly of secondary quartz resulting  
155 from a post-depositional silicification and recrystallization of translucent dolomite and chert  
156 clasts, also resulting from a late secondary recrystallization with an extensive carbonatization.  
157 These three samples contain also ankerite, silicified dacitic ash, illite-sericite mixed layers and  
158 some chlorite clay-type minerals. All selected samples host also accessory apatite, monazite  
159 (rhabdophane), zircon and Cr-Spinel, together with minor pyrite that seems to be of primary  
160 biogenic origin. A barite-rich vein observed in sample FTG3 testifies for the occurrence of  
161 tectonic activities (Fig. 2). Similar to the FTG1 sample, the FTG1a and b samples were  
162 collected in its close vicinity as local “duplicates”.

163

## 164 **The analytical procedure**

165         Petrographic and stratigraphic descriptions, as well as isotopic data of the selected  
166 untreated whole rocks were already published (Toulkeridis et al., 1998). Rb-Sr, Sm-Nd and  
167 Pb-Pb dated, these rocks provide isochrons with isotopic ages of  $2,632 \pm 99$  Ma,  $2,612 \pm$   
168  $84$  Ma and  $2,743 \pm 36$  Ma, respectively. Significantly younger than the estimated depositional

169 age of  $\sim 3,260 \pm 20$  Ma, these ages were considered to reflect a late combined silicification  
170 and sericitization at an apparent temperature of  $\sim 200^\circ\text{C}$ . Silicified after deposition, the  
171 carbonate minerals represent only up to 50 % of sample FTG1, while the other samples  
172 contain less (Table 1). In fact, several thermal events that affected the entire belt after  
173 deposition of the Fig Tree sediments (Weis and Wasserburg, 1987; De Ronde et al, 1991;  
174 Kamo and Davis, 1993; de Ronde and de Wit, 1994; Tice et al., 2004; Hofmann, 2005;  
175 Toulkeridis et al., 2010) obviously modified the mineral compositions of these rocks.

176 In fact, leaching techniques are applied for long, especially on clay materials of  
177 various environments with a variety of isotopic methods (e.g., Bofinger et al., 1968;  
178 Chaudhuri and Brookins, 1979; Morton and Long, 1980; Clauer, 1981; Bros et al., 1992;  
179 Clauer et al., 1993; Toulkeridis et al., 1998; Zhao et al., 1999; Clauer and Chaudhuri, 2012),  
180 while sedimentary whole rocks were leached less often, except those of Precambrian age for  
181 stratigraphic purposes. The reason for such leaching experiments is the separate analysis of  
182 the soluble and residual minerals for a differentiated evaluation of the alteration, weathering  
183 and/or re-crystallization minerals (e.g., Sahuquillo et al., 2003). It may also be recalled at this  
184 point that the real new aspect of the herein experiment is the successive leaching of the same  
185 rocks (for the initial leaching) and residues (for the following steps) by using progressively  
186 stronger reagents, which means that the further interactions did not concern the previously  
187 dissolved minerals. It might also be recalled that the prerequisite for a successful leaching  
188 experiment is in a systematic alignment of the data points of the untreated (labeled U),  
189 leachable (labeled L) and residual (labeled R) fractions of the same separates, whatever the  
190 meaning of the obtained alignment. The necessary array is clearly a matter of chemical  
191 equilibrium among the different separates and not a matter of the analyzed material. A  
192 determining advantage of such experiments is in the improved meaning of the leached  
193 concentrates by individual analyzes of their elemental contents and isotopic compositions.  
194 The relative contents allow more accurate chemical compositions for the soluble minerals  
195 mixed with the insoluble silicate minerals in the rocks, including those of economic interest  
196 identified by their trace metals. These leachable elements may result from flowing fluids that  
197 transported and concentrated specific elements during post-depositional tectonic-thermal  
198 events before incorporation into contemporaneous soluble minerals or adsorption onto  
199 insoluble minerals.

200 Here, the successive leaching steps were also used to evaluate the impact of the  
201 different reagents on the different types of soluble minerals, and on the residues that were  
202 expected to remain inert to the reagents. In the experiences completed here, about two grams

203 of powdered sediment were leached successively with distilled water (H<sub>2</sub>O), 1N acetic acid  
204 (HAc), 1N hydrochloric acid (HCl) and 1N nitric acid (HNO<sub>3</sub>), during 15 minutes at room  
205 temperature. De-ionized H<sub>2</sub>O and ultra-pure reagents were used at all steps of the sample  
206 preparation. While H<sub>2</sub>O and the HAc and HCl acids at a 1N concentration are considered as  
207 weak reagents with no substantial impact on any siliceous minerals (e.g., Clauer et al., 1993),  
208 HNO<sub>3</sub> is highly corrosive even at a 1N concentration with a possible impact on the silicate  
209 minerals, at least on the sensitive clay minerals. The amounts of dried powder and liquid  
210 reagent were precisely measured at each leaching step for consistent comparisons. After each  
211 step, the residues were dried gently and a given amount of each was taken and digested in a  
212 mixture of HF + HNO<sub>3</sub> + HClO<sub>4</sub> + HCl in Teflon© beakers. The major, trace and rare-earth  
213 elements (labeled REEs hereafter) were determined for both the leachates and the residues of  
214 each leaching step, together with the Sr and Nd isotopic compositions. In order to reduce as  
215 much as possible the analytical blanks, and therefore a potential analytical contamination of  
216 Pb, the whole procedure was processed with smaller amounts of sample and acids.

217 The elemental contents of the four whole rocks were determined on an inductively  
218 coupled plasma atomic emission spectrometer (ICP-AES of the Centre de Géochimie de la  
219 Surface of the Strasbourg University) for the majors (Al, Si, Ca, Mg, Fe, Mn and P) and one  
220 trace element (Sr), and on an inductively coupled plasma mass spectrometer (ICP-MS of the  
221 same laboratory) for two trace (Rb and Pb) and the rare-earth elements (REEs). Repeated  
222 analysis of the international standards B-EN and GL-O on a weekly basis provided an overall  
223 analytical precision of  $\pm 2.5\%$  ( $2\sigma$ ) for the major elements,  $\pm 5\%$  for the trace elements and  
224  $\pm 10\%$  for the REEs, on the basis of the analytical procedure by Samuel et al. (1985).

225 The Sr isotopic analyses were obtained on a multi-collector mass spectrometer (VG  
226 Sector of the same Strasbourg laboratory). The Sr separation was based on a chemical  
227 procedure identical to that of Schaltegger et al. (1994). The <sup>87</sup>Sr/<sup>86</sup>Sr ratio of the NBS987  
228 standard was of  $0.710254 \pm 0.000012$  ( $2\sigma$  external,  $n = 6$ ) at the time of the study. For the  
229 isochron calculations, an average uncertainty of  $\pm 0.000015$  ( $2\sigma$ ) was assumed for the  
230 <sup>87</sup>Sr/<sup>86</sup>Sr ratio on the basis of the standard reproducibility, whereas the accuracy of the  
231 <sup>87</sup>Rb/<sup>86</sup>Sr ratios was better than  $\pm 2.5\%$  ( $2\sigma$ ). The <sup>87</sup>Rb/<sup>86</sup>Sr of a few FTG1 leachates and  
232 residues were duplicated by a complete preparation and analysis for an overall control of their  
233 reproducibility. All <sup>87</sup>Sr/<sup>86</sup>Sr ratios were corrected relative to 0.1194 for the <sup>86</sup>Sr/<sup>88</sup>Sr ratio of  
234 the NBS987 standard.



235 All Sm-Nd isotopic analyses were completed on two Finnigan MAT 261 mass  
236 spectrometers (of the Max-Planck Institut für Chemie of the Mainz University Germany). The  
237 REEs were separated following the procedure of White and Patchett (1984). The  $^{143}\text{Nd}/^{144}\text{Nd}$   
238 ratios were normalized to 0.7219 for the  $^{146}\text{Nd}/^{144}\text{Nd}$  ratio. During the study, the value of the  
239  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of La Jolla Nd standard was  $0.511882 \pm 0.000012$  ( $2\sigma$  external,  $n = 10$ ). For  
240 the isochron calculation, a routine uncertainty of  $\pm 0.000012$  ( $2\sigma$ ) was assumed for the  
241 measured  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios on the basis of reproducibility of the standard. If the internal  
242 error of a single isotope analysis was larger than  $\pm 0.000020$  ( $2\sigma$ ), the higher value was  
243 used. The  $^{147}\text{Sm}/^{144}\text{Nd}$  of a few FTG1 leachates and residues were also duplicated with a  
244 complete sample preparation and analysis to control their reproducibility, while a routine  
245 uncertainty of  $\pm 2.0\%$  ( $2\sigma$ ) was taken for the age calculations. All  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios were  
246 corrected relative to the La Jolla standard  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of 0.511860.

247 The Pb isotope ratios were determined in a static mode on a Finnigan MAT-261 mass-  
248 spectrometer (of the Max-Planck Institut für Chemie of the Mainz University, Germany). The  
249 Pb was purified following a standard ion exchange technique (Krogh, 1973), and was  
250 measured with a mixture of phosphoric acid and Si-gel (Cameron et al., 1969) on single Re  
251 filaments. The Pb isotopes were measured individually and the Pb isotopic ratios were  
252 corrected for a mass fractionation factor of 0.1% per a.m.u., which was determined by  
253 measuring the NBS982 (Todt et al., 1996). If the internal error of an individual analysis was  
254 higher than the error defined by the  $2\sigma$  value of the NBS 982, the higher value was used.

255 The analytical uncertainties for the alignments obtained by the three isotopic methods  
256 were calculated on the basis of Ludwig's (2003) Isoplot program and were given with the  
257 results when they appeared to be realistic and useful. The Mean Square Weight Deviates  
258 (MSWDs) that report how well more than two data points fit any correlation line are also  
259 provided when the age data of the drafted arrays were meaningful on the basis of the isochron  
260 calculations. In turn, MSWD values validate isochron lines whether the errors are of  
261 analytical or geological functions (Brooks et al., 1972). Although random variations in  
262  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios induce increases of the associated MSWDs, Davidson et al. (2005) discussed  
263 how age data remain geologically meaningful even with higher MSWD values derived from  
264 variations induced by open-system mixing or contamination. Such variations can result from  
265 nicely fitting arrays but with geologically meaningless ages. In such cases, if ages are  
266 determined via varied isotopic techniques, the calculated  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios may provide a further  
267 insight into the petrogenetic processes resulting in the mixing of Sr with different origins.

268 Therefore, alignments based on somewhat scattered analytical data points from successive  
269 leaching steps, but with age values reasonably close to the ages obtained by associated  
270 isochrons, or to those obtained with other leachates and/or residues by the same or by the  
271 other isotopic methods, were not considered here as strict isochron lines but rather as trends  
272 with ages close to those of the isochrons but with uncertainties beyond the isochron  
273 reproducibility. These trends were tentatively called “isotrends” hereafter and not  
274 “errorchrons” in the sense of McIntyre et al (1966), as they are not defined on the basis of  
275 numerical calculations. In fact, they were only taken into account when their age values were  
276 within the uncertainties given by the independent associated isochrons.

277

## 278 **The results**

279 Leaching with H<sub>2</sub>O provided the lowest dissolution amounts with releases between  
280 0.12% and 0.42% of the initial whole-rock weights (Table 1). Conversely, the most efficient  
281 leaching was that with HCl that removed about 31% of the initial weight, followed by HAc  
282 that dissolved about 24%, both of the FTG1 sample. Leaching with HNO<sub>3</sub> dissolved only very  
283 small amounts of the left-over rock powders, with soluble separates of 0.5 to 1.2% of the  
284 sample weights after the already removal of the “ss” leachable material. The FGT1 sample  
285 was the most sensitive to the successive leaching steps with a global removal of 55%. The  
286 FTG2 and FTG3 samples were affected the less with about 18% of their initial weight  
287 removed, while the FTG4 sample lost slightly more of its initial weight at 21%.

288

### 289 *The contents of the major elements*

290 All leachates were analyzed for their contents in Al, Si, Ca, Mg, Fe, Mn and P that were  
291 expressed as elemental ratios (Table 2). The reagents were chosen to have each a specific  
292 impact on the selected whole rocks: the sequence started with H<sub>2</sub>O thought to dissolve  
293 preferentially the potential salts and to remove elements adsorbed on the mineral surfaces.  
294 Then HAc was chosen to remove the Mg- and Fe-carbonates and the Fe-sulfates, followed by  
295 HCl to dissolve the phosphates and the reminders of the Ca-carbonates. The last reagent was  
296 HNO<sub>3</sub> mainly to oxidize any potential organic matter, which was expected to be low in such  
297 old rocks with a possible side impact on fragile silicate components due to its high toxicity.  
298 The elemental concentrations removed by H<sub>2</sub>O were very low relative to Si taken as the  
299 immobile reference representative of the insoluble silicates. The elements removed the most  
300 by H<sub>2</sub>O were systematically Mg and Ca with ratios beyond unity relative to the

301 “conservative” Si (Table 2). The highest Ca and Mg contents with the highest Ca/Si and  
302 Mg/Si ratios were obtained for the samples FTG1 and FTG3, the lowest being for sample  
303 FTG2. In fact, the leachates were mostly Ca-loaded for all samples, while also enriched in Fe  
304 for those of the samples FTG3 and FTG4. The contents of the HCl leachates are quite similar  
305 to those of the FTG1 and FTG2 HAc leachates, while lower than those of the FTG3 and  
306 FTG4 samples. The only significant contents of Ca, Mg and Fe in the HNO<sub>3</sub> leachates were  
307 obtained for the FTG3 and FTG4 samples.

308 The most removed Ca, Mg and Fe record the dissolved minerals with equivalent Ca  
309 and Mg amounts leached from FTG1 sample, about 2.7 times more Ca than Mg leached from  
310 FTG2 sample and similarly 3.3 and 2.5 times more Ca than Mg from FTG3 and FTG4  
311 samples (Fig. 2). The contents of Fe are far less: 150 to 300 times less than Ca in sample  
312 FTG1, about 550 times less in samples FTG2 and FTG4 and about 1390 times less in sample  
313 FTG3. By comparing the Ca/Si, Mg/Si and Fe/Si ratios of the four FGT1 H<sub>2</sub>O leachates, the  
314 overall patterns are very similar with only the ratios changing (Fig. 2). In turn, the interactions  
315 were quite similar for all samples with apparently equivalent mineral compositions and  
316 changes only significant in the soluble amounts.

317 In sum, the four rocks are quite similar for their main mineral compositions with  
318 differences in the detail of each. The Ca contents are higher than those of Mg and Fe in the  
319 H<sub>2</sub>O leachates, while high Ca/Si ratios in the HAc and HCl leachates rather point to soluble  
320 Ca-minerals. The high Fe/Si ratios suggest the occurrence of Fe-rich minerals, mostly in  
321 sample FTG3. Leaching by HNO<sub>3</sub> appears only efficient in sample FTG3 and very attenuated  
322 in sample FTG4, while the high Mg/Si ratios probably correspond to soluble Mg-minerals,  
323 whereas the equivalent amounts of Mg and Ca correspond probably to dolomite that was  
324 detected independently in the rocks (Fig. 3A).

325

### 326 *The contents and the distribution patterns of the rare-earth elements*

327 The REE concentrations of the untreated whole rocks range from 24.4 µg/g in sample  
328 FTG1 to 133.3 µg/g in sample FTG2, those of the two other FTG3 and FTG4 samples being  
329 of 58.2 and 67.6 µg/g, respectively (Table 4). The REE contents decrease progressively in the  
330 successive leachates. With less than 0.4% of the initial rock weight, the impact of the H<sub>2</sub>O  
331 leaching was not evaluated further as the variations were not expected to be really  
332 representative relative to the ±10% analytical uncertainty. The next leaching by HAc was also  
333 almost undetectable in the total REE contents being between 1 and 0.1 µg/g lower than those  
334 of the untreated rocks, which again is quite difficult to evaluate with the ±10% analytical

335 uncertainty (Table 3). The HCl step removed 20.4% REEs from initial content of sample  
336 FTG1, while only 2.8% from that of sample FTG2, 3.6% from that of sample FTG3 and 7.4%  
337 from that of sample FTG4. The final HNO<sub>3</sub> leaching removed 38.8% from initial REE content  
338 of sample FGT1, 10.4% from that of sample FTG2, 14.9% from that of sample FTG3 and  
339 19.2% from that of sample FTG4.

340 The amounts of the heavy REEs (labeled hereafter HREEs) increase in the residues of  
341 the HAc leaching, while the HNO<sub>3</sub> leachates are enriched in HREEs with a Gd/Yb ratio up to  
342 three times that of the corresponding residues. The fact that the HAc leaching did not induce  
343 any decrease of the total amounts of REEs in any of the four samples implies that the  
344 dissolved minerals were notably depleted in REEs. The following HCl leaching removed  
345 20.8% REEs from FTG1 sample, as well as 3.4%, 2.7% and 7.4% from FTG2 to FGT4  
346 samples, successively. The final HNO<sub>3</sub> leaching removed 18.7% REEs of sample FTG1, 7.5%  
347 of sample FTG2, 9.5% of sample FTG3 and 11.8% of sample FTG4.

348 It might be quickly recalled that REE distribution patterns of geological materials are  
349 often compared to a standard/reference material. Here, the patterns of the successive leachates  
350 were compared to that of standard chondrites (Evensen et al., 1978), which is a usual choice  
351 for Precambrian sedimentary materials because both the analyzed rocks and the standard  
352 material are often of similar types and origins. In fact, younger sedimentary rocks are more  
353 often compared to either the North-American Shale Composite (NASC; Gromet et al. 1984)  
354 or the Post-Archaean Australian Shales (PAAS; Taylor and McLennan, 1985). There is no  
355 fundamental difference about comparing the REE contents of sediments and metasediments  
356 with any of these three references, except that it is easier to visualize variations of a flat  
357 pattern such as those relative to the PAAS and/or NASC and not relative to an inclined one  
358 like that of the chondrites. The REE contents and distribution patterns of Fig Tree shales were  
359 already analyzed by McLennan et al. (1983) who found that they are characterized by variable  
360 patterns with high La/Yb ratios of  $5.5 \pm 1$ , which corresponds to an inclined pattern towards  
361 less HREEs. Relative to the chondrite reference, all untreated whole rocks and all  
362 corresponding residues yield here similar inclined decreasing REE distribution patterns with a  
363 positive Eu anomaly and a smooth incurved end for the heaviest REEs (Fig. 4A). In the detail,  
364 the patterns of the FTG2 and FTG4 samples are similar, whereas that of sample FTG1 is more  
365 widely scattered with a positive Tm anomaly and that of sample FTG3 yields a negative Tm  
366 anomaly (Fig. 4B). These different Tm contents refer, most probably, to analytical aspects due  
367 to very small contents at the detection limit of the used equipment.

368 When compared to the PAAS patterns, those of the untreated samples, the residues  
369 and the leachates are quite similar (Fig. 4B). In the detail, only the amounts are changing with  
370 patterns showing a very constrained light REE (labeled LREE hereafter) distribution until Sm,  
371 then a significant positive Eu anomaly with an intensity depending on the type of used  
372 reagent. From Eu to Lu, the HREEs give again a flat pattern but with a more dispersed  
373 distribution than that of the LREEs. In fact, only the HNO<sub>3</sub> leachates yield very low contents  
374 with, however, a pattern relatively similar to the solid and liquid aliquots. In the detail, the  
375 patterns of the leachates show significantly lower contents from La to Sm and from Gd to Lu  
376 relative to those of the untreated whole rocks and of their residues. Those of the leachates are  
377 also less inclined towards the HREEs, while more scattered relative to the chondrite reference  
378 (Fig. 4C). Only those of the FTG1 sample yield a pronounced positive Eu anomaly, as for the  
379 other residues. This Eu anomaly is changing in the different leachates of the same FTG1  
380 sample: highest in that by HNO<sub>3</sub> leaching and lowest in that by HCl leaching. The HNO<sub>3</sub>  
381 leachates yield systematically the lowest REE contents, with the most positive Eu anomaly for  
382 the pattern of sample FTG1. Highest in the HCl leachates, this anomaly relates to the  
383 systematic occurrence of Ca-carbonates in the four samples, except in the HNO<sub>3</sub> leachate  
384 where no Ca-carbonate remains and for which it cannot be excluded that it suggests a silicate  
385 alteration by the reagent.

386 In summary, the REE distribution patterns relative to either the chondrites or the  
387 PAAS are not intrinsically determining in the delineation of the mineral compositions and the  
388 historic evolution of their host rocks. However, they are helpful in decrypting the intensity of  
389 the impacting events. The patterns relative to the PAAS are quite similar from lightest to the  
390 heaviest REE except the systematic variation in the Eu anomaly (Fig. 4). Close to that of the  
391 untreated sample, the highest Eu anomalies are those of the residues after the H<sub>2</sub>O leaching.  
392 The next highest Eu anomalies are, then, those of the HAc, HCl and HNO<sub>3</sub> residues. In the  
393 case of the leachates, the highest Eu anomaly is that of the HAc leachate, followed by those of  
394 the HCl and HNO<sub>3</sub> leachates.

395

### 396 The Rb-Sr isotopic data

397 The <sup>87</sup>Sr/<sup>86</sup>Sr ratios of the residues increase systematically after each leaching step,  
398 while those of the leachates become less radiogenic after the successive H<sub>2</sub>O, HAc and HCl  
399 leaching steps (Table 5) and are widely dispersed for the HNO<sub>3</sub> residues. The reagents alter  
400 differentially the constituting minerals of the initial rocks, as the variations do not result from  
401 analytical problems. Indeed, six analytical differences amongst two independent analyses of

402 the same  $^{87}\text{Rb}/^{86}\text{Sr}$  ratio were below  $\pm 3.1\%$  ( $2\sigma$ ); only the reproducibility of the  $\text{HNO}_3$   
403 experiments was higher at  $\pm 3.7\%$  and  $\pm 9.0\%$  ( $2\sigma$ ; Table 5). Also, the plot of the untreated,  
404 leachate and residue aliquots along single arrays in isochron diagrams guaranty well-done  
405 experiments without any loss of any of the components from the separates (Fig. 5), the next  
406 step depending then on how the obtained arrays can be identified as isochrons with  
407 meaningful ages.

408 Due to the extremely limited amounts of elements removed by the  $\text{H}_2\text{O}$  leaching, the  
409 corresponding residues can be assimilated to the untreated samples, with the HAc leachate  
410 and residue data points fitting the same array, for instance in the case of the FTG1 and FTG2  
411 samples. The data points of the HCl leachate and residue of sample FTG2 plot slightly above  
412 and below the array drawn through the HAc leachate and residue data points (Fig 5). On the  
413 other hand, the data points of the  $\text{HNO}_3$  leachate and residue of sample FTG1 are dispersed  
414 away from the two arrays. In the case of sample FTG3, the lower array with the lowest slope  
415 includes the data points of the HAc leachate and residue, while the upper line integrates the  
416 data points of the two HCl leachates with a nearby data point of the  $\text{HNO}_3$  residue.  
417 Furthermore, the data point of the  $\text{H}_2\text{O}$  residue plots just below the lower array, together with  
418 that of the untreated rock. The results of sample FTG4 are slightly scattered with a similar  
419  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for the HAc, HCl and  $\text{HNO}_3$  leachates, together with an unexpected high  
420  $^{87}\text{Rb}/^{86}\text{Sr}$  ratio for the  $\text{HNO}_3$  leachate. The HCl residue yields very high ratios, while the data  
421 point of the untreated rock (in red) plots slightly below the line joining the data points of the  
422 HCl leachate and residue.

423 The ages and the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were calculated for the arrays of the four  
424 samples (Fig. 5). The lower of the two lines obtained for sample FTG1 are based on the HAc  
425 leachate and the data points of the untreated and  $\text{H}_2\text{O}$  leached whole rock. It yields an age  
426 value of  $2,182 \pm 47$  Ma (MSWD = 0.95) for an initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.7062 \pm 0.0002$ . The  
427 array above consists of one HAc leachate, one HCl leachate and one  $\text{HNO}_3$  residue that  
428 appears to be an heterogeneous assemblage as the  $\text{HNO}_3$  leachate is clearly away from the  
429 other data points, especially from other leachates with an abnormal high  $^{87}\text{Rb}/^{86}\text{Sr}$  ratio.

430 The results of FTG2 sample raise an interesting duality between the data points of the  
431 HCl leachate and residue and a  $\text{HNO}_3$  residue that give a high age value of  $2,971 \pm 64$  Ma  
432 (MSWD = 0.02) and an initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.7093 \pm 0.0003$ . The two data points of the  
433 HAc leaching give a second array with the untreated whole rock (in red) and a  $\text{H}_2\text{O}$  residue  
434 with a significantly lower age value of  $2,222 \pm 41$  Ma (MSWD = 2.2) that is within the age  
435 range of the FTG1 data. The data points of the untreated whole rock of sample FTG3 with the

436 H<sub>2</sub>O residue and the HAc leachate give a further isochron array with a close age of  $2,461 \pm 51$   
437 Ma (MSWD = 1.5) and an initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.7143 \pm 0.0001$ . To be mentioned also is  
438 the very high initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of  $0.7243 \pm 0.0003$ , far above the  $0.7062 \pm 0.0002$  obtained  
439 for the array fitting the HCl data of the FTG1 sample and giving a similar age. The difference  
440 between the data of the HAc and the HCl leachates is confirmed by the results of the same  
441 FTG3 and FTG4 leachates. The arrays through the HCl data points also provide  
442 systematically the highest age values in both cases, being even unrealistic beyond 3.8 Ga. The  
443 initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the HAc and HCl arrays are also significantly different; that of the  
444 HCl lines range narrowly from about 0.706 to 0.709, while that of and with the HAc leachates  
445 varies widely from about 0.706 to 0.724. The HNO<sub>3</sub> leachate of FTG3 sample yields the  
446 almost lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio for the almost highest  $^{87}\text{Rb}/^{86}\text{Sr}$  ratio.

447 In summary, leaching with dilute HCl and HAc does not provide similar results for both  
448 the leachates and the residues. Obviously, the two experiments did not remove the same  
449 soluble minerals, which was expected by the sequential mode unless they dissolved identical  
450 minerals but of different chemical compositions and necessarily of different generations. The  
451 HCl leaching gives arrays that yield systematically steeper slopes and, consequently, higher  
452 age values than those of the corresponding HAc leaching. Some of these age values are even  
453 unrealistic, beyond the probable deposition age of the Fig Tree sediments, which favors an  
454 identification of mixing lines and not isochrons. In this case the HCl leaching probably  
455 affected at least the retention capabilities of other soluble minerals than the plain carbonates.  
456 A further remark is for the HNO<sub>3</sub> leaching that gives either similar or very different  $^{87}\text{Sr}/^{86}\text{Sr}$   
457 ratios for the leachates and the residues, depending on the leached samples. This strongly  
458 suggests that the reagent dissolved minerals of a composition similar or even identical to that  
459 of the insoluble residual minerals, unless altering slightly some fragile silicate minerals with a  
460 few release of Rb and Sr. On the basis of the strict analytical results, the HAc leaching  
461 provided several times age data of about 2.2 and 2.9 Ga as solid age references, with also a  
462 collective age of  $2,799 \pm 42$  Ma for all the residues.

463

#### 464 The Sm-Nd isotopic data

465 The trends of the leachate and residue data points obtained by the Sm-Nd system are  
466 similar to those of the Rb-Sr method (Table 5; Fig. 6), the main difference being in the  
467 respective locations of the data points in an isochron diagram. In contrast to those of the Rb-  
468 Sr system, the leachates yield higher  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios than their corresponding residues and,  
469 therefore, plot farther away from the array origins than the residues (e.g., Bros et al., 1992).

470 There is another difference along with the Rb-Sr method, namely the analytical precision of  
471 the Sm-Nd isochron ages that strongly depends on the  $^{143}\text{Nd}/^{144}\text{Nd}$  spread of the separates  
472 due to the limited disintegration of the  $^{147}\text{Sm}$ . Here, the quite narrow spread in the  
473  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio from 0.09 to 0.22 with large errors of the age data are then, together with  
474 small MSWDs, indicative of satisfying analytical conditions. Also to be mentioned is the  
475 analytical uncertainty between three analyses of the same  $^{147}\text{Sm}/^{144}\text{Nd}$  found to be below  
476  $\pm 2.9\%$  ( $2\sigma$ ) except for the HCl and  $\text{HNO}_3$  experiments which data range at  $\pm 4.2\%$  and  
477  $\pm 8.3\%$ , respectively ( $2\sigma$ ; Table 5). It has then been decided to provide hereunder all the  
478 analytical errors for completeness, not considering all of them in the comparisons with the  
479 other isotopic results and in the discussion about the age meaning (Fig. 6).

480 The data points of five FTG1 residues, the three HAc residues and the HAc and HCl  
481 residues fit an array with an age value of  $2,002 \pm 140$  Ma (MSWD = 2.1) and an initial  
482  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.5095 \pm 0.0002$  ( $2\sigma$ ). An alignment through the data points of the FGT2  
483 HAc and HCl leachates and of the  $\text{H}_2\text{O}$ , HAc, HCl and  $\text{HNO}_3$  residues yields an age value of  
484  $2,831 \pm 560$  Ma (MSWD = 4.3) with a large uncertainty and an initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio at  
485  $0.5086 \pm 0.0005$  ( $2\sigma$ ). The sample FTG3 yields the same display with the same leachate and  
486 residues data points for another close age of  $2,930 \pm 290$  Ma (MSWD = 0.03), a large  
487 uncertainty and an identical initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.5086 \pm 0.0003$  ( $2\sigma$ ). The two HCl  
488 points fit a slightly steeper array with an age value of  $3,343 \pm 440$  Ma and an initial  
489  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.5082 \pm 0.0004$  ( $2\sigma$ ). Finally, the two HAc and the two HCl data points,  
490 together with those of the untreated whole-rock and the  $\text{HNO}_3$  residue of sample FGT4 fit an  
491 array with an age value of  $3,922 \pm 490$  Ma (MSWD = 0.25) for an initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  
492  $0.5078 \pm 0.0004$  ( $2\sigma$ ), which is unrealistic because of the theoretical deposition age of the  
493 sedimentary sequence and because of its large uncertainty. The complementary HCl line  
494 through the leachate and residue data points yields a far younger age data of  $1,444 \pm 180$  Ma  
495 for an initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.5083 \pm 0.0003$ . This is the only significantly younger age  
496 value obtained here, but as the array was drawn only through two data points it is of weak  
497 constrain.

498 In summary, leaching with HCl and HAc does not provide similar Sm-Nd ages as was  
499 already the case for the Rb-Sr method, which confirms indirectly that the reason is in the  
500 samples, not in the methods. Also, the Sm-Nd age values of sample FTG4 give unrealistically  
501 high and low values, while the  $\text{HNO}_3$  leaching provides unexpectedly similar  $^{147}\text{Sm}/^{144}\text{Nd}$



502 ratios for the leachates and the residues, as was also the case for the Rb-Sr method. About the  
503 strict analytical data, one average age value concentrates at 2.9 Ga.

504

#### 505 The Pb-Pb isotopic data

506 The H<sub>2</sub>O residues of the four FTG samples were analyzed by the Pb-Pb method,  
507 together with the HAc, HCl and HNO<sub>3</sub> leachates and the HAc and HNO<sub>3</sub> residues of the  
508 FGT1 and FGT4 samples (Table 6). The <sup>206</sup>Pb/<sup>204</sup>Pb ratio decreases for the successive  
509 leachates of sample FTG3, while the HNO<sub>3</sub> leachates of the other three samples became more  
510 radiogenic. In an isochron diagram, the data points range along trends, however not precisely  
511 enough to allow age calculations with reasonable uncertainties. In fact, only four data points  
512 of sample FTG4, three leachates and one residue, plot along an array that yields an age value  
513 of 2,032 ± 48 Ma (MSWD = 2.5; Fig. 7A). In fact, the Pb-isotopic data of the leachates and  
514 residues from the four samples scatter around two major trends (Fig. 7B): an upper one  
515 includes only the data points of sample FTG1 and a steeper one with the data points of the  
516 other samples. These Pb-isotopic data outline more or less parallel arrays that were tentatively  
517 identified as “isotrends” with average ages and acceptable uncertainties, like for the two other  
518 methods, rather than “isochrons” with more constrained ages and uncertainties. The  
519 differences between well-defined isochrons and less-defined isotrends may then be due to: (1)  
520 the fact that soluble Pb yields variable isotopic compositions due to various origins and/or  
521 mineral combinations, or to recent altering contamination(s), (2) a potential contamination  
522 during the handling and preparation of the samples that can also not be excluded, and (3) a  
523 variable natural Pb-isotope composition, especially in the leachates, suggesting a variable  
524 alteration of metal-rich rocks subjected to a natural metal alteration. However, some of the  
525 Pb-Pb ages, such as that at 2,032 ± 48 Ma, set reliable milestones and, consequently, are not  
526 supportive of a continuous natural contamination by metallic ore concentrates.

527

#### 528 **Discussion**

529 The collective Rb-Sr data of the H<sub>2</sub>O residues organize into an alignment that can be  
530 assimilated to an isochron with an age of 2,799 ± 42 Ma that fits well with the 2,632 ± 99 Ma  
531 for the previously published isochron of the untreated whole rocks (Toulkeridis et al., 1998).  
532 The very gentle action of H<sub>2</sub>O explains this proximity as a surface cleaning of the constitutive  
533 minerals. Despite large analytical errors due to the limited spread of the Sm/Nd ratio, the  
534 corresponding ages for the HAc and HCl residues are close to that of the untreated rocks,

535 while the results of the HNO<sub>3</sub> leaching are unexpectedly scattered and therefore questionable.  
536 In fact, the Sm-Nd method provides the above identified isotrends rather than isochrons  
537 because of the slight mentioned spread of the Sm/Nd ratio, but further isotrends with  
538 significant errors can also be identified. The H<sub>2</sub>O leachates and residues of the FTG2 to FTG4  
539 samples give Pb-Pb isochrons, while those of sample FTG1 rather fit the just defined  
540 isotrends. These less precise alignments confirm that the Pb-Pb data suggest different  
541 elemental sources or generations for soluble Pb-carrying minerals, unless an unexpected  
542 analytical aspect needs consideration. The main question becomes then the identification of  
543 the different compositions of the soluble leachates and of the residues after the interaction  
544 with each reagent.

545 As already mentioned, published stratigraphic ages are often based on single leaching  
546 experiments with single-method ages, by combining the data of multiple untreated rocks or  
547 minerals, sometimes with the corresponding leachates and residues. Indeed, the assumption  
548 for such attempts was, admittedly, the age value of the data identifying a supposed event  
549 (deposition, diagenesis or metamorphism) responsible for the isotopic homogenization of the  
550 used isotopic system. Designed as a multi-control of leachates and residues subjected to a  
551 long and complex history, therefore with varied mineral compositions, the method consists  
552 here to identify the traces and the epochs of the successive impacting events on the basis of  
553 distinguishing various dissolved minerals and residues. A preliminary comment is about the  
554 obtained isotopic data that give, whatever the isotopic system, less precise alignments than  
555 usual isochrons that were tentatively replaced by the above defined “isotrends”. The analytical  
556 dispersion of these isotrends seems to be due to limited but sensitive variations in the  
557 chemical and also in the isotopic compositions of the constitutive minerals with various  
558 reactions depending on the used reagents (Fig. 8). It may also be mentioned that minor  
559 analytical problems can never be excluded completely along the sample preparation and  
560 spectrometric analysis, even if most variations obtained here seem to be due to natural and not  
561 analytical aspects.

562

### 563 *The isotopic “ages” of the leachates*

564 The graphical distribution of the data points from untreated whole rocks provides an  
565 initial alignment with noticeable differences in the Sr contents of the samples. Sample FTG1  
566 yields clearly an overwhelming content of Sr relative to an <sup>87</sup>Rb/<sup>86</sup>Sr ratio below 0.5. On the  
567 other hand, the FTG3 and FTG4 samples consist of more insoluble minerals giving an  
568 <sup>87</sup>Rb/<sup>86</sup>Sr ratio above 3, which is close to that of sample FTG2 (Fig. 9C). These differences

569 result from varied lithofacies of the samples, confirmed in turn by the Ca/Si ratio of the HCl  
570 leachates that is to say by the ratio of the soluble relative to the insoluble minerals. This Ca/Si  
571 ratio is of 50.4, 14.5, 121 and 14.5 for the four FTG1 to FTG4 samples, respectively. The  
572 highest ratio of 121 for sample FTG3 with, by far, the highest Fe/Si ratio corroborates the  
573 occurrence of a Fe-rich soluble phase.

574 The comparison of the Rb-Sr results from leachates shows that those of sample FTG1  
575 by HAc plot very narrowly (Fig. 9A and B). This plot confirms that the leaching experiments  
576 were completed correctly within analytical uncertainty, and that the analytical dispersion of  
577 the leachates from the other samples are due to natural mineralogical heterogeneities of the  
578 rocks. Dispersed relatively to those of the HAc leachates, the equivalent HCl and HNO<sub>3</sub> data  
579 result from dissolution of minerals that were necessarily heterogeneous in their Sr isotopic  
580 composition. Consequently, the array through the data points of the untreated whole rocks is  
581 not a true isochron but rather a mixing line because of that lack of Sr isotopic homogeneity.  
582 Also to be noticed are the identical trends for the HCl and HAc leachates of the FTG1 to  
583 FTG3 samples (Fig. 5).

584 On the basis of the Rb-Sr results, it is clear that the untreated rocks contain soluble  
585 minerals that reacted variably depending on the used reagent. Sample FTG1 reacts to HAc  
586 with leachates loaded in Ca and consists therefore mostly of Ca carbonates, while the HCl  
587 leachates are loaded in Fe and therefore of probable Fe-enriched carbonates and/or sulfates.  
588 The fact that the HCl leachates give arrays with steeper slopes suggests that the Fe-rich  
589 minerals may be older than the other minerals, or that they were subjected to a lower degree  
590 of remobilization/recrystallization than the Ca-rich counterparts. On the other hand, the age  
591 values of the HCl separates may yield age values older than the probable deposition age of the  
592 Fig Tree sediments, suggesting in turn that some of these carbonates could even contain  
593 relicts of detrital origin, but which is not realistic for soluble minerals that are expectedly  
594 sensitive to any post-depositional thermal alteration. It could also be that leaching removed  
595 also Rb off the corresponding residues that decreased their Rb/Sr ratio and consequently  
596 increased their corresponding age values. The conclusion about the HNO<sub>3</sub> leaching impact is  
597 also not immediate, as it provides similar <sup>87</sup>Sr/<sup>86</sup>Sr ratios for the leachates and the residues  
598 with unexpected high <sup>87</sup>Rb/<sup>86</sup>Sr ratios for the leachate of samples FTG1 and FTG4, together  
599 with a high <sup>87</sup>Sr/<sup>86</sup>Sr ratio for the latter. The identical <sup>87</sup>Sr/<sup>86</sup>Sr ratios for both the leachate and  
600 the residue also point toward a congruent dissolution of residual material with <sup>87</sup>Sr/<sup>86</sup>Sr ratios  
601 similar to those of the leachates.

602 The Sm-Nd data points of the HAc and HCl leachates plot also on separate  
603 alignments, as do those of the HNO<sub>3</sub> leachates (Fig. 10). All these lines yield increasing  
604 positive slopes with increasing Sm/Nd ratios. The “curvy” organization of the four lines  
605 through the leachate points has already been identified as an analytical prove for  
606 heterogeneous materials: the HNO<sub>3</sub> leachates build the lower branch of the composite curve,  
607 while the HAc line represents the intermediate trend of the curve and the HCl line the upper  
608 section. None of these arrays yields meaningful stratigraphic ages, as the HCl and HAc  
609 leachates of sample FTG3 plot even outside the lines through the leachate points. In fact, they  
610 plot quite narrowly but on two lines with data points of residues, as will be discussed in a  
611 further section. The age data calculated for sample FTG4 give unrealistically high values  
612 beyond the admitted deposition time of the sediments, while the HNO<sub>3</sub> leaching gives,  
613 surprisingly, similar <sup>147</sup>Nd/<sup>144</sup>Nd ratios for the leachates and the residues. The Pb-Pb results  
614 of the FTG2, FTG3 and FTG4 leachates can be organized into three sub-parallel isotrends  
615 consisting of heterogeneous separates. The age values are of  $2,800 \pm 260$  Ma (MSWD = 8.2),  
616  $2,850 \pm 760$  Ma (MSWD = 4.2) and  $2,749 \pm 490$  Ma (MSWD = 12.0) for the three arrays  
617 consisting each of four data points. It is very tempting to suggest that these data focus on a  
618 unique tectonic-thermal event that occurred at about  $2.8 \pm 0.5$  Ga.

619 In summary, the overall Rb-Sr, Sm-Nd and Pb-Pb results suggest that two important  
620 events occurred in this region of the Barberton Greenstone Belt at  $2.9 \pm 0.1$  and  $2.1 \pm 0.1$  Ga,  
621 as well as one or several less intruding episodes between 1.6 and 2.0 Ga (Table 7). These  
622 milestones are also confirmed by several isotrends giving similar age values but with large  
623 uncertainties.

624

#### 625 The isotopic “ages” of the residues

626 Taken together, the Rb-Sr data of the residues show an incurved distribution with a  
627 changing angle for the upper HAc data points (Fig. 11A). Such a display characterizes  
628 heterogeneous materials, either as whole rocks or as size fractions (e.g., Clauer et al., 2020).  
629 When plotted in the same diagram, all data points of the residues organize into distinct  
630 patterns resulting from either “gentle” H<sub>2</sub>O and HAc leaching on the lower linear branch, or  
631 from HNO<sub>3</sub> leaching on a sub-parallel linear trend above the previous one, whereas that of the  
632 HCl reagent gives the upper display (Fig. 10A). The consequence is that these results,  
633 especially those of the HCl leaching, yield age values that are geologically meaningless. Once  
634 again, sample FTG3 contains a heterogeneous component clearly reactive to the HCl  
635 leaching.

636 The Rb-Sr age calculations of the different residues give several arrays (Fig. 11A).  
637 That based on three residues of the HNO<sub>3</sub> leaching yields a high isotrend age value of about  
638  $3,754 \pm 710$  Ma (MSWD = 26) with a high analytical uncertainty. On the lower side, the data  
639 points of five H<sub>2</sub>O residues fit a line with an age of  $2,799 \pm 42$  Ma (MSWD = 0.04) and an  
640 initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio of  $0.7009 \pm 0.0007$ . This value may, again, be considered as meaningful  
641 with an acceptable initial Sr ratio for such old sediments. The data points of more H<sub>2</sub>O  
642 residues fit a sub-parallel isotrend with a similar age of  $2,764 \pm 240$  Ma.

643 The Sm-Nd data of all residues were also combined in a single isochron diagram (Fig.  
644 10B). The HNO<sub>3</sub> residues of sample FTG1 yield the flattest trend, while those of the three  
645 other samples fit an independent line, also with a very low slope. By contrast, most data  
646 points of the H<sub>2</sub>O and HAc residues plot on an array with an age of about 2.9 Ga and an initial  
647 <sup>143</sup>Nd/<sup>144</sup>Nd ratio of about 0.5086, the large errors suggesting again an isotrend. The data  
648 points of the FTG3 and FTG4 residues plot narrowly, also on an isotrend with a slope sub-  
649 parallel to the previous one.

650 The Pb-Pb data of the residues plot on an array with a steep slope (Fig. 7), but which  
651 data points are widely scattered, and therefore with a high uncertainty. In fact, these results do  
652 not add much to the already available age values obtained by the Rb-Sr and Sm-Nd methods.  
653 However, the Pb-Pb age between 2.75 and 2.85 Ga is confirmed by the already published Rb-  
654 Sr and Sm-Nd results of the residues.

655

#### 656 Meaning of the leachate-residue "ages"

657 The data of the sequential leaching support the hypothesis that the whole rocks studied  
658 here contain various soluble minerals that react variably depending on the used reagent.  
659 About the calculated age values, the alignment of the HAc leachates and residues of FTG1  
660 sample provides a Rb-Sr isochron representative of the Ca-carbonate at  $2,182 \pm 47$  Ma, also  
661 obtained for sample FTG2. On the basis of given mineral contents from the rock suite, the  
662 purpose becomes a stepwise separation of soluble phases in order to quantify their  
663 compositions and, therefore, sort out their specific histories. The determination of the REE  
664 contents was expected to support the identification of individually dissolved minerals. In turn,  
665 it cannot be excluded that beyond the dissolution of the soluble minerals and surface cleaning  
666 of the insoluble minerals, some of these silicate minerals were also altered slightly especially  
667 by the HNO<sub>3</sub> leaching. It may explain the high or at least unusual radiogenic signatures for  
668 some of the arrays (e.g., Fig. 5 and 6) for which the obtained age values are also older than the  
669 depositional age. It cannot, furthermore, be ignored that the obtained results suggest also

670 potential detrital provenances. Given the results, the Archaean rocks could have also been  
671 subjected during their long and disrupted evolution to some contamination/pollution, not by  
672 the present-day atmosphere but during the tectonic-thermal episodes that might have induced  
673 some scattering by long-distance migrations of exotic fluids. This could especially have been  
674 the case for the Pb-Pb method highly dependent on a strict closed behavior of the metal  
675 carriers.

676 In summary, the combined application of the Rb-Sr, Sm-Nd and Pb-Pb dating methods  
677 on various types of leachates and associated residues of a few samples enabled to contribute  
678 to the reality of isotopic ages at  $2.9 \pm 0.1$  and  $2.1 \pm 0.1$  Ga for the studied Fig Tree  
679 metasediments (Table 7). On the basis of the data of the classical untreated whole-rock  
680 technique (Touleridis et al. 1998), these ages probably resulted from large-scale fluid  
681 movements generated by successive tectonic-thermal activities already described elsewhere.  
682 The slightly older 2.4-Ga age obtained by  $^{40}\text{Ar}/^{39}\text{Ar}$  ages of altered barite from Barberton  
683 Greenstone Belt (De Ronde et al., 1991) was only obtained here by an isotrend and could be  
684 part of either the start or the end of the two longer and better constrained tectonic-thermal  
685 episodes around. Indeed, the 2.0 Ga age obtained more or less precisely by the Sm-Nd method  
686 on sample FTG1 is correlative with the emplacement of the Bushveld complex and other  
687 intrusive complexes in the Kaapvaal Craton. It was obtained previously by  $^{40}\text{Ar}/^{39}\text{Ar}$  dating of  
688 sedimentary rocks (De Ronde et al., 1991) and biotites of surrounding granodiorites (Layer et  
689 al., 1992), as well as by Rb-Sr dating of cherts (Weis and Wasserburg, 1987). It propagated  
690 most probably at a quite low closing temperature of  $\sim 130^\circ\text{C}$  with some quartz  
691 recrystallization. Also not formally confirmed by a Rb-Sr age of sample FTG1, the younger  
692 age at  $\sim 1.7$  Ga was unknown as a widespread event in the Kaapvaal Craton, but was reported  
693 previously by  $^{40}\text{Ar}/^{39}\text{Ar}$  dating of highly altered basaltic pillows (Layer et al., 1992).

694

#### 695 *The isotopic results of the variously leached rocks*

696 Identical ages obtained by various isotopic methods after leaching different types of  
697 whole rocks appear appropriate to distinguish evolution steps of especially old rocks that  
698 underwent multiple tectonic-thermal impacts of varied intensities. The geologically  
699 meaningful ages at  $2.9 \pm 0.1$  and  $2.1 \pm 0.1$  Ga obtained here on various carbonated rocks  
700 supports the reality of these two historic milestones in the early evolution of the Archaean  
701 carbonate-rich Fig Tree samples. Also, the isotopic methods applied at different leachates and  
702 residues provided also some isotrends that comfort the isochron ages with larger uncertainties.  
703 Therefore, leachates obtained by different reagents that give reasonably close ages even if less

704 constrained confirm that: (1) the use of reagents of variable intensity combined with different  
705 isotopic methods is appropriate; (2) isotrends do not necessarily result from analytical  
706 problems; and (3) the ages obtained by the isotrends help constrain age data given by  
707 identified isochrons. As a further comment, it looks like the Pb-Pb method is the less adequate  
708 of the used isotopic methods for such attempts as the data scatters could also be contaminated  
709 by external facts due to the natural behavior of Pb isotopes. In turn, it cannot be excluded that  
710 the analytical Pb-Pb dispersion was also impacted by the regional metalliferous context of the  
711 samples and result from labile behavior of Pb during a multi-composite evolution and/or  
712 possibly to a recent to present-day pollution that would need to be identified.

713 The initial isotopic ratios of the isochrons and the isotrends from leachates may also  
714 provide information about the chemistry of the interacting fluids. The initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios  
715 are often dispersed between 0.706 and 0.720, including the initials of the arrays giving  
716 unrealistic old age data. It looks like the authigenic soluble minerals of the successive  
717 tectonic-thermal events yielded variable Sr isotopic signatures that relate to the signatures of  
718 the potential interacting fluids. For instance, the arrays of about 2.8-2.9 Ga were obtained  
719 with initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios at  $0.7093 \pm 0.0003$  ( $\pm 2\sigma$ ),  $0.7143 \pm 0.0001$  and  $0.7200 \pm 0.0004$ .  
720 Conversely, the initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of the alignments are consistently narrower for each  
721 isochron or isotrend. Those of the lines with slopes about 2.8-2.9 Ga are at  $0.5086 \pm 0.0005$   
722 ( $\pm 2\sigma$ ) and  $0.5086 \pm 0.0003$ , and that of the line at about 2.1 Ga is of  $0.5095 \pm 0.0002$  ( $\pm 2$ ).  
723 The limited number of Pb-isotopic data does not allow such a comparison of the initial ratios  
724 of the Pb-Pb arrays.

725 In summary, the initial ratios of the isochrons and of the isotrends provide basics for  
726 the Rb-Sr and the Sm-Nd methods. The Sr isotopic identity of the Rb-Sr method is quite  
727 dispersed, whereas the Nd identity of the Sm-Nd method is much more concentrated,  
728 therefore focusing on different compositions, origins and possibly temperatures for the  
729 associated fluids. The Rb-Sr isotopic “world” appears much more heterogeneous than that of  
730 the comparative Sm-Nd system. However, it is actually difficult to relate these types of results  
731 to precise events and processes that are as old as 2.8 Ga.

732

### 733 *The evolution of the Kaapvaal Craton based on the data of the leachates*

734 The overall similar REE distribution patterns of the residues suggest that the silicates  
735 yield narrowly similar mineral compositions, except for a more diversified assemblage for  
736 sample FTG1, for which the successive residues of the same FTG1 sample yield, however,  
737 very close patterns (Fig. 4B). Furthermore, the systematic positive Eu anomaly detected in the

738 leachates and the residues of the samples analyzed here excludes, in turn, its traditional  
739 relation with the occurrence of detrital plagioclase feldspars, but operates rather as a function  
740 of temperature and oxygen fugacity (Weill and Drake, 1973). The reason for the abnormal  
741 occurrence of Eu resulted then from: (1) tectonic-thermal episodes that altered feldspars of the  
742 meta-sediments, or (2) released REEs disseminated in various types of minerals including  
743 soluble ones. In fact, MacRae et al. (1992) reported positive Eu anomalies in diagenetically  
744 impacted sediments with Eu considered to precipitate in the  $3^+$  state when the environment  
745 was of oxidation potential. Just before, Bau (1991) predicted that oxygen fugacity increasing  
746 with the temperature, the fluid-rock interactions under mild acidic conditions favor a positive  
747 anomaly. Nakada et al. (2019) showed also that positive Eu anomalies can occur when water  
748 interacted with the rocks at hydrothermal conditions below 100°C. Along the study of this  
749 positive Eu anomaly in Precambrian sediments, Banded Iron Formations older than 2.5 Ga  
750 from various sites of North America, Finland and Australia were found to yield positive Eu  
751 anomalies, while younger ones did not (Danielson et al., 1992; Bolhar et al., 2004). The  
752 former authors also stated that the anomaly seems to be dominantly driven by hydrothermal  
753 conditions with solution temperatures above 175°C. Kato et al. (1996) reported also positive  
754 Eu anomalies in Banded Iron Formations of India and suggested that they were of  
755 hydrothermal origin. In summary, the positive Eu anomaly seems to have been driven by low-  
756 temperature oxidizing hydrothermal conditions in Banded Iron Formation older than 2.5 Ga.  
757 The widely tectonic-thermal events described in the craton and dated isotopically appear,  
758 therefore, as favorable conditions to the occurrence of the Eu anomaly detected in the soluble  
759 and insoluble mineral phases studies here.

760         The large number of geochronological studies on South-African Archaean meta-  
761 sediments has shown that the whole Barberton Greenstone Belt was affected by several  
762 tectonic-thermal events during its complex evolution. Based on the literature, five events were  
763 identified at ~3.45, 3.25, 3.1, 2.7, and 2.1–2.0 Ga (e.g., Weis and Wasserburg, 1987; Lopez-  
764 Martinez et al., 1992; Kamo and Davis, 1994; Lécuyer et al., 1994). The ~2.7-Ga episode  
765 dated here by applying simultaneously the Rb-Sr, Sm-Nd and Pb-Pb methods on various  
766 leachates and residues of silicified carbonated rocks points to a wide regional extend. The  
767  $^{40}\text{Ar}/^{39}\text{Ar}$  age at  $2,673 \pm 3$  Ma of a barite from the same locality as the rocks studied here was  
768 reported by De Ronde et al. (1991) with a release temperature of Ar at ca. 200°C. It  
769 consolidates the thermal impact suggested by the positive Eu anomaly of the REE patterns.  
770 However, the importance of this event does not exclude the potentiality of an even earlier  
771 tectonic-thermal episode predicted by Hofmann (2005). It is significant in this respect, that



772 clay minerals separated from the same samples as those studied here provided a Sm-Nd  
773 isochron age of  $3,102 \pm 64$  Ma, while their Rb-Sr and K-Ar systems were affected later at  
774 about 2.05 Ga (Toulkeridis et al., 1998). This younger 2.05 Ga age was obtained here by the  
775 three methods, in fact between 2.07 and 2.45 Ga and mostly by data of leachates.  
776 Interestingly, the older limit at 2.45 Ma obtained by a Rb-Sr isochron of sample FTG3  
777 corresponds somewhat to  $^{40}\text{Ar}/^{39}\text{Ar}$  ages of altered barite (De Ronde et al., 1991). The next  
778 younger age at  $\sim 1.6$  Ga was confirmed here by a Rb-Sr isochron of FTG1 aliquots, and as for  
779 the event at 2.4 Ga, this age was set by  $^{40}\text{Ar}/^{39}\text{Ar}$  ages of altered basalt pillows. (Layer et al.,  
780 1992) that looks more as a local volcanic episode out of the regional context.

781

## 782 **Conclusions**

783

784 Based on a sequential leaching of silicified Archaean carbonates from Kaapvaal  
785 Craton, the chemical data and Rb-Sr, Sm-Nd and Pb-Pb isotopic ages show that the  
786 successive dilute HAc, HCl and HNO<sub>3</sub> acids interacted with soluble minerals of variable  
787 chemical compositions. Application of the isotopic dating methods on the untreated, leached  
788 and residual whole rocks also contributed to the reconstruction of the complex post-  
789 depositional evolution of these Archaean rock-forming minerals. Already published isotopic  
790 ages of  $2.7 \pm 0.1$  and  $2.3 \pm 0.2$  Ga were obtained again by combining the various leachates  
791 and/or residues resulting from different reagents. These leachates also yielded a systematic  
792 positive Eu anomaly and, therefore, resulted from large-scale fluid movements generated by  
793 wide regional tectonic-thermal activities during the two dated events. Multiple analyses of  
794 solid and soluble aliquots generate sometimes multiple sub-parallel isotopic trends tentatively  
795 identified as isotrends with constitutive data points that are slightly more scattered than those  
796 of the associated isochrons, confirming in turn age values within the analytical uncertainties  
797 of the associated isochrons.

798 The younger event set here at about  $1.6 \pm 0.1$  Ga could relate to the emplacement of  
799 the Bushveld complex and/or other intrusive complexes of the Kaapvaal Craton. Similar ages  
800 that probably represent closure temperatures of the Fig Tree sediments at about 200°C and  
801 less, correspond to identical REE distribution patterns that were already reported elsewhere in  
802 and around the craton.

803

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805

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824

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826

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## 1117 **Figure and Table captions**

1118

1119 **Figure 1:** Sample location near the city of Barberton within the Barberton Greenstone Belt  
1120 (after Toulkeridis et al., 1998). The central map is located as a rectangle on the sketch of  
1121 South Africa in the upper left corner with the states of Swaziland and Lesotho. The red star  
1122 locates the sampling places. The dashed line to the right is the boundary between the South  
1123 African Transvaal and the Swaziland.

1124 **Figure 2:** The Ca/Si, Mg/Si and Fe/Si ratios of the successive H<sub>2</sub>O, HAc, HCl and HNO<sub>3</sub>  
1125 leachates from studied samples. The different colors of the symbols represent the different  
1126 types of leachates.

1127 **Figure 3:** Scanning-electron microscopic pictures of the FTG samples; (A) idiomorphic  
1128 dolomite crystals in the matrix of sample FTG1 surrounded by a fine-grained layer of illite-  
1129 type crystals; (B) a barite-rich vein crosscutting sample FTG3; (C) a blow up of the FTG1  
1130 matrix with elongated illite and squared quartz crystals; (D) A blow-up of a dolomite  
1131 crystal in the FTG1 matrix. The pictures A to C are from Toulkeridis et al. (1998).

1132 **Figure 4:** Chondrite and PAAS normalized REE patterns of: (A) the untreated FTG whole  
1133 rocks; (B) the FTG1 residues after each leaching step; (C) the FTG1 leachates after each

1134 leaching step. Most duplicated residues and leachates being extremely similar, only one of  
1135 each has been portrayed.

1136 **Figure 5:** Rb-Sr patterns of the leachates and residues of the four FTG samples by the  
1137 successive reagents. The four untreated whole-rock data are in red. The shapes and colors  
1138 of the symbols stand for the four displays. The age values of the arrays are given along the  
1139 respective alignments together with the initial ratios.

1140 **Figure 6:** Sm-Nd patterns for the leachates and residues of the four FTG samples for the  
1141 successive reagents. The shapes and colors of the symbols stand for the four displays. The  
1142 age values of the arrays are given along the respective alignments.

1143 **Figure 7:** Pb-Pb diagrams obtained by the interactions of the successive reagents identified by  
1144 the same symbols in each display. The shape and color of the symbols stand for the four  
1145 displays.

1146 **Figure 8:** Two examples of Sm/Nd (in A) and Pb/Pb (in B) isotrends. The shape and color of  
1147 the symbols stand for the two displays.

1148 **Figure 9:** Rb-Sr diagrams of the leachates (in A and B) and of the untreated whole rocks (in  
1149 C) of the four FTG samples. The diagram B is a blow up of display A. The colors of the  
1150 symbol stand for the two A and B diagrams and the numbers in the three diagrams  
1151 correspond to the samples.

1152 **Figure 10:** Sm-Nd patterns of the leachates (A) and residues (B) of the four FTG samples  
1153 identified by the colored symbols to the lower right side of the upper pattern. The symbol  
1154 shapes and colors in the upper pattern correspond to the types of aliquots.

1155 **Figure 11:** Rb-Sr displays of all residues in diagram (A) and those of the different residues  
1156 (B1 to B4) of each FTG sample. The colored symbols and the numbers in the diagram (A)  
1157 correspond to the four FTG samples. The symbols in the B diagrams correspond to the  
1158 same aliquots.

1159

1160

1161 **Table 1:** Calculated percentages of the leachates and the residues by the different reagents of  
1162 the four Fig Tree samples. The indices a and b stand for the duplicate samples collected  
1163 near the FGT1 sample.

1164 **Table 2:** Ratios by weight of the major elements of the leachates obtained by the successively  
1165 used H<sub>2</sub>O, HAc, HCl and HNO<sub>3</sub> reagents on the four samples. The indices a and b stand  
1166 for the duplicate samples collected near the FTG1 sample.

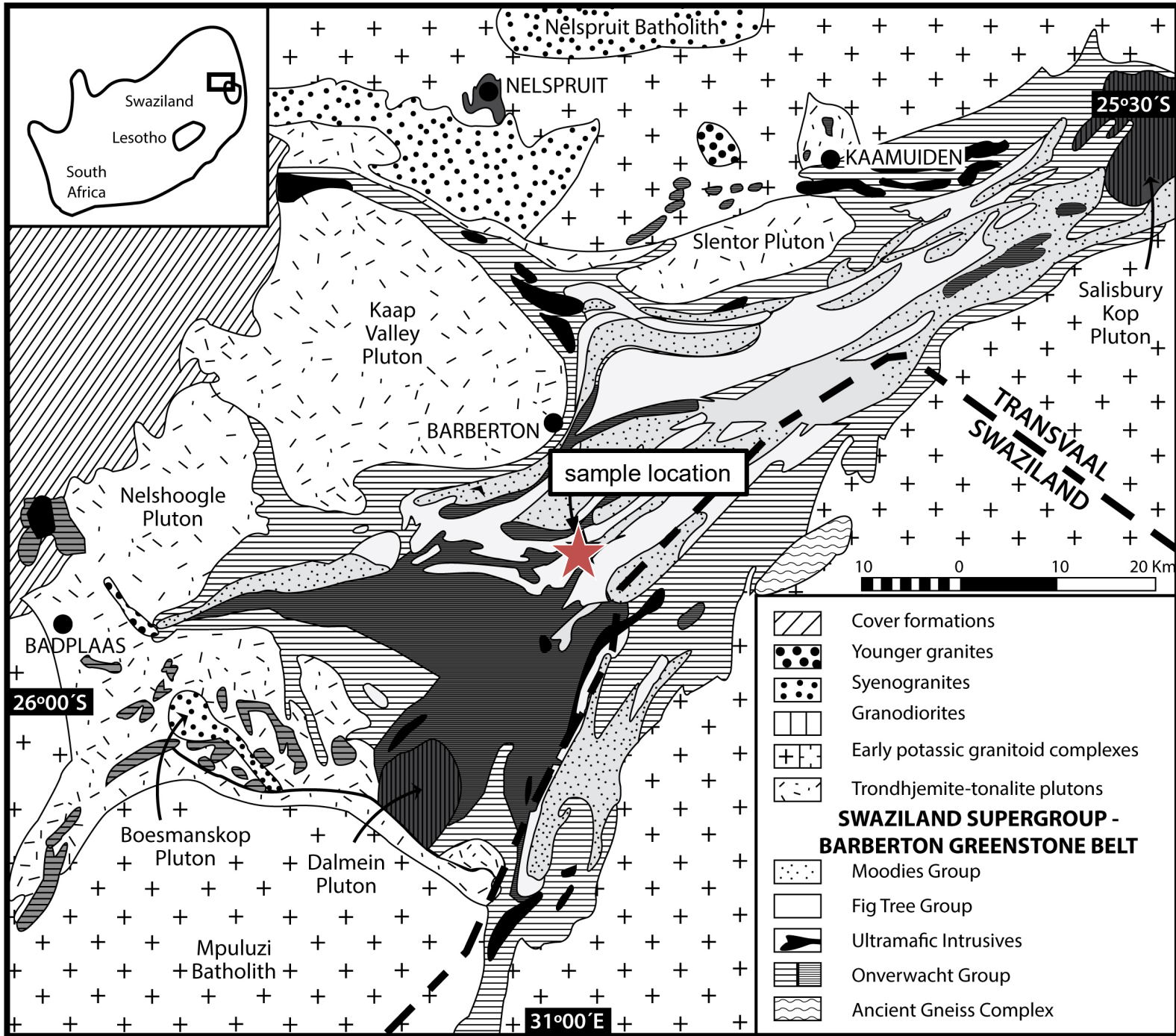
1167 **Table 3:** Amounts of REEs leached off the four FTG samples by the successive reagents. The  
1168 total contents are in  $\mu\text{g/g}$ .

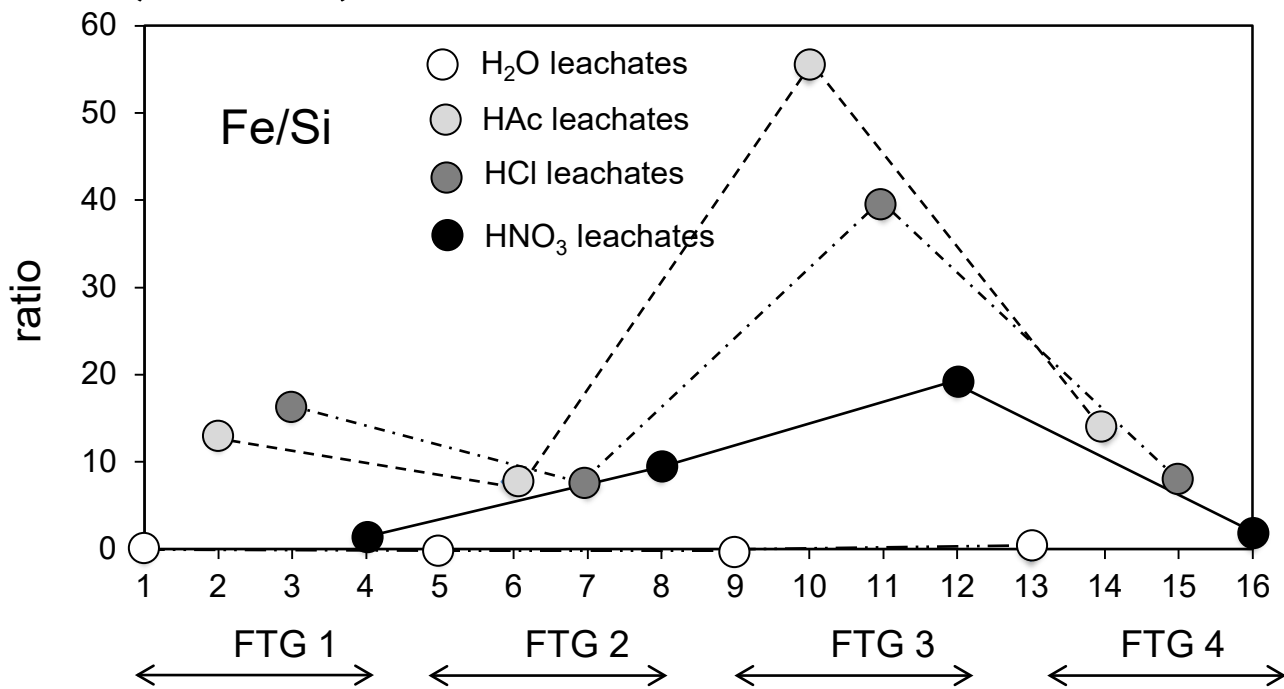
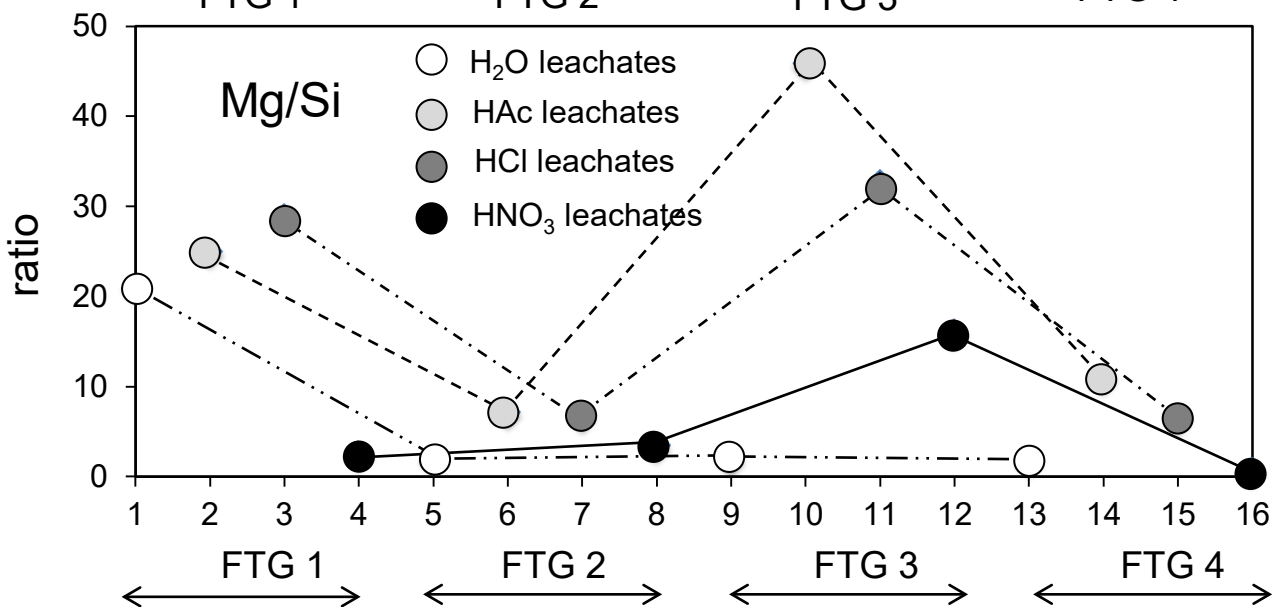
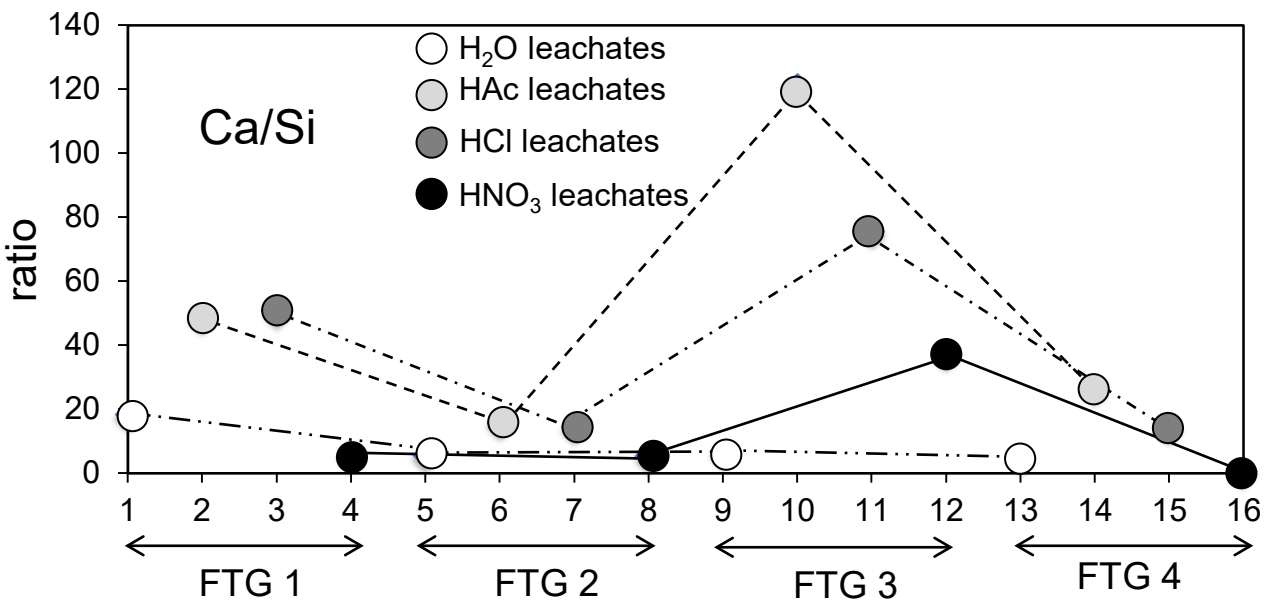
1169 **Table 4:** The rare-earth elemental contents of the leachates (labeled L) and residues (labeled  
1170 R) after the successive HAc, HCl and HNO<sub>3</sub> leaching steps of the four samples. WR stands  
1171 for whole rocks and the indices a and b of sample FTG1 stand for the duplicate samples  
1172 collected nearby.

1173 **Table 5:** The Rb-Sr and Sm-Nd isotopic data. WR corresponds to whole rocks, L to leachates  
1174 and R to residues of each H<sub>2</sub>O, HAc, HCl and HNO<sub>3</sub> reagent. The indices a and b stand for  
1175 the duplicate samples collected near the sample FTG1.

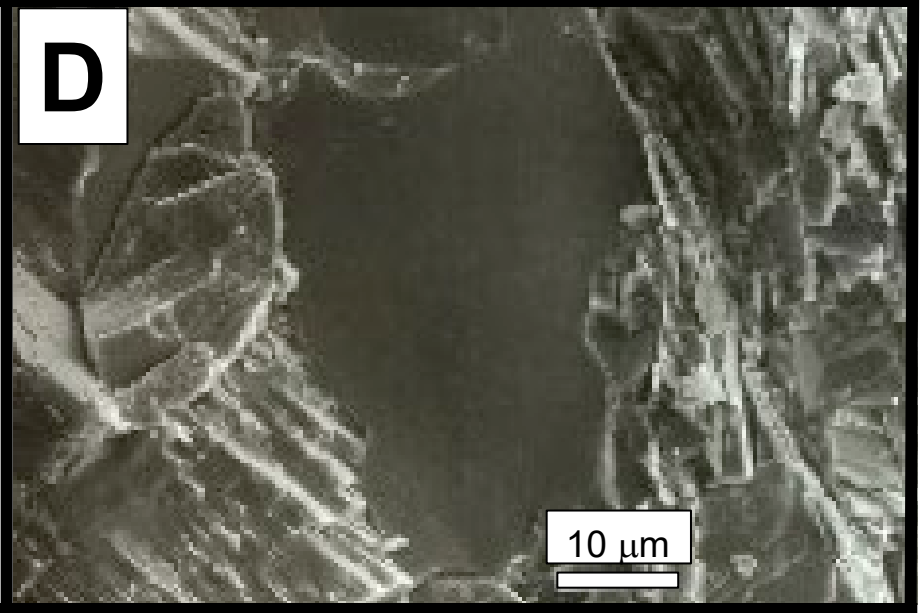
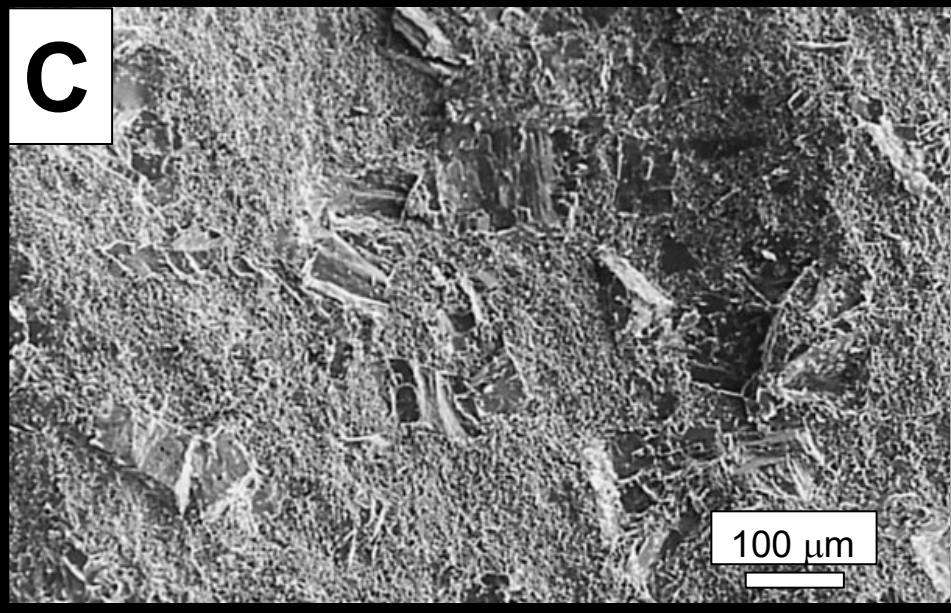
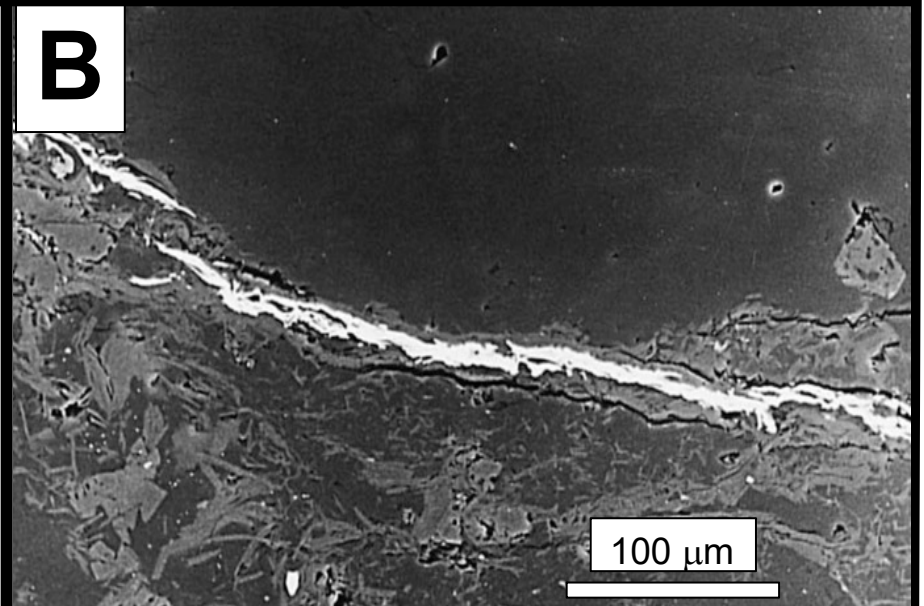
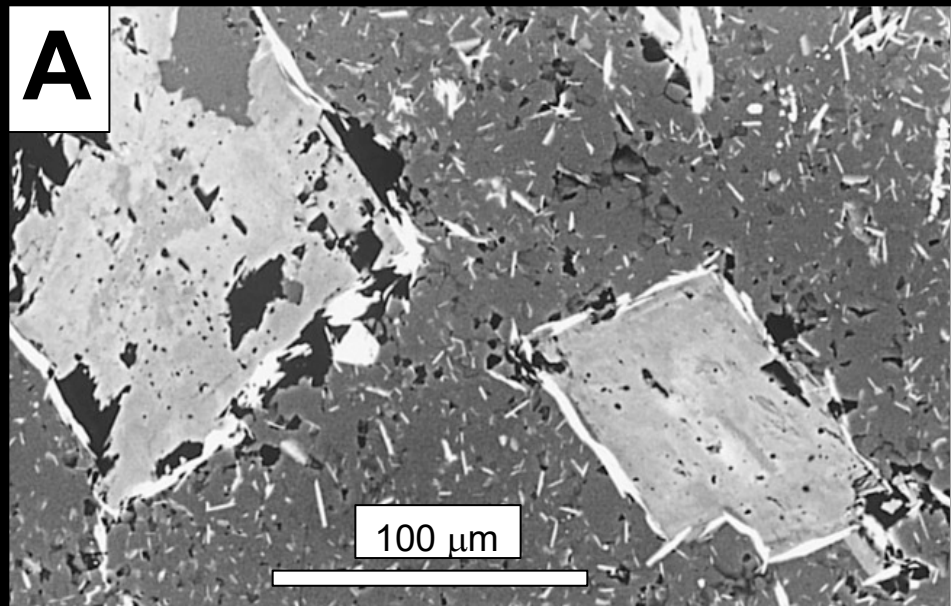
1176 **Table 6:** The Pb-Pb isotopic data with the  $\pm 2\sigma$  uncertainties.

1177 **Table 7:** A summary of the Rb-Sr, Sm-Nd and Pb-Pb age values obtained for the isochrons  
1178 and isotrends of the four FTG samples. The numbers in brackets relate to independent age  
1179 calculations for each method and sample, while leach stands for leachates. The numbers in  
1180 bold stand for each major isochron result.

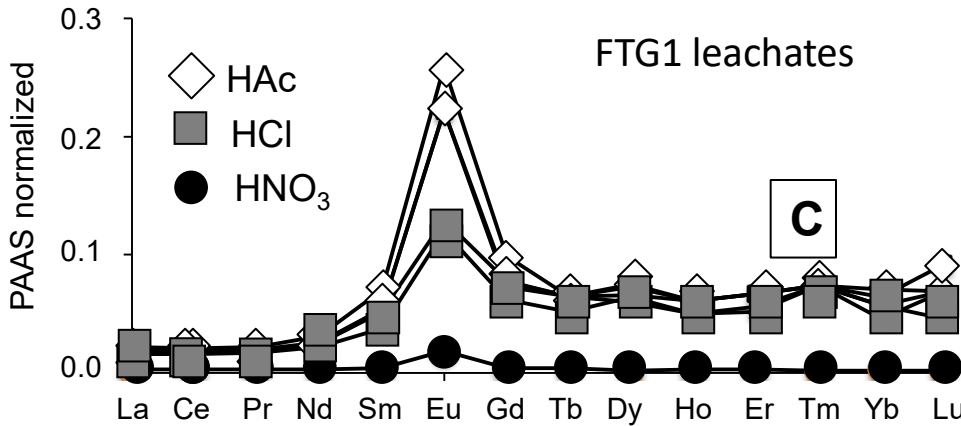
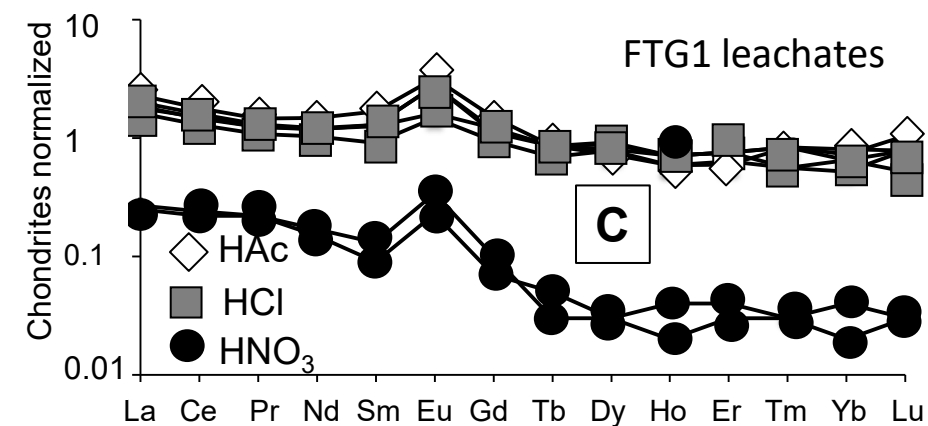
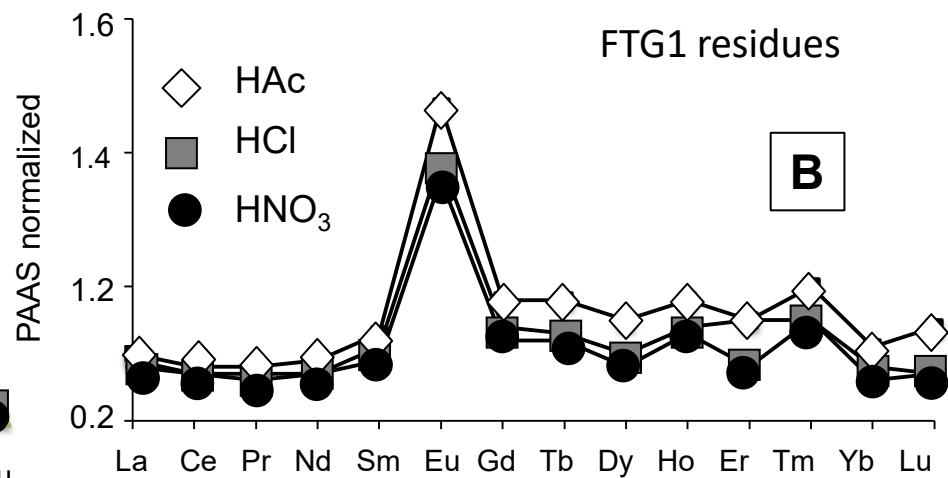
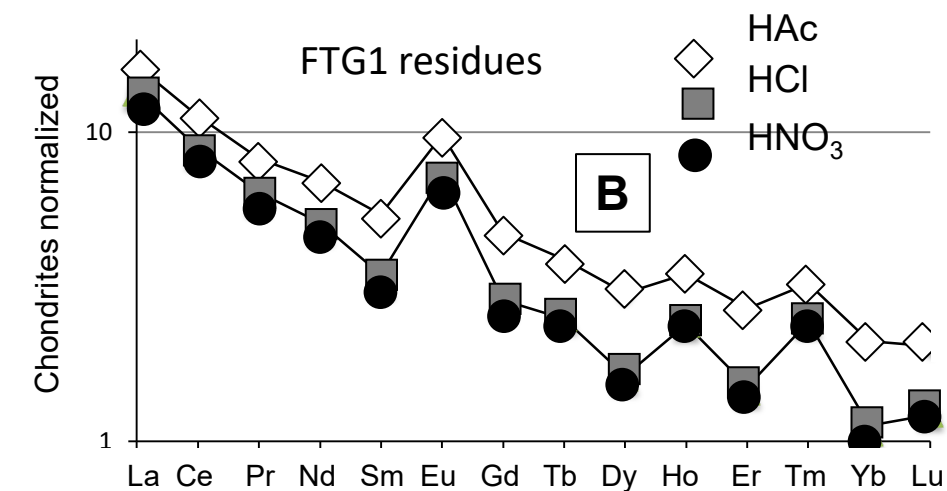
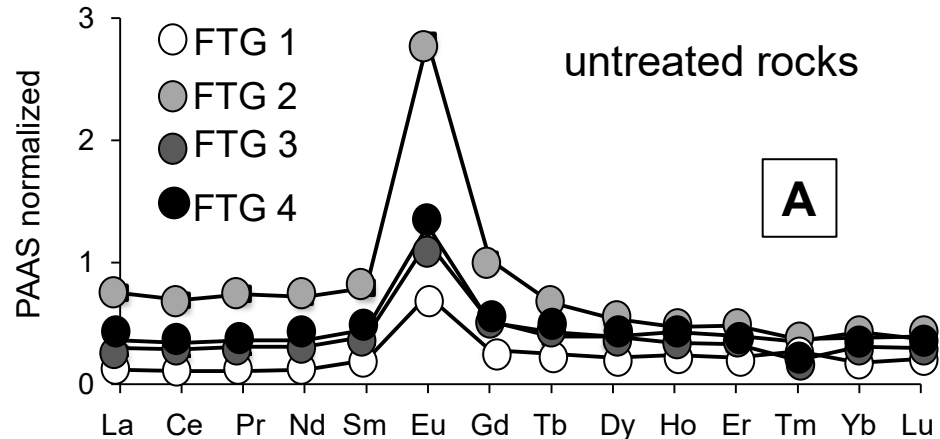
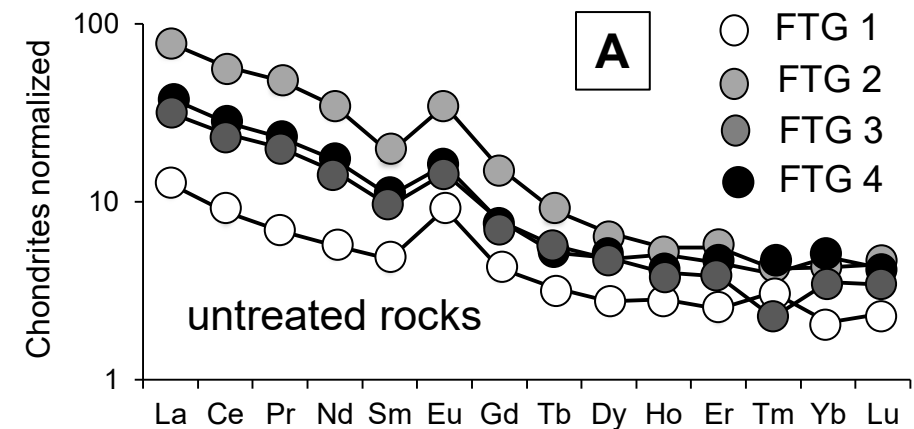


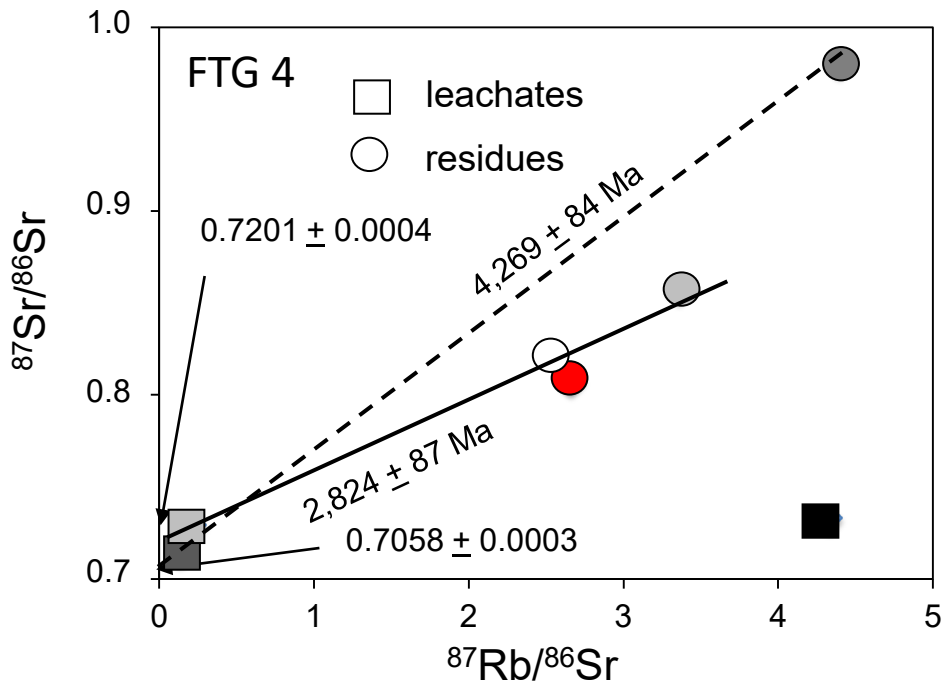
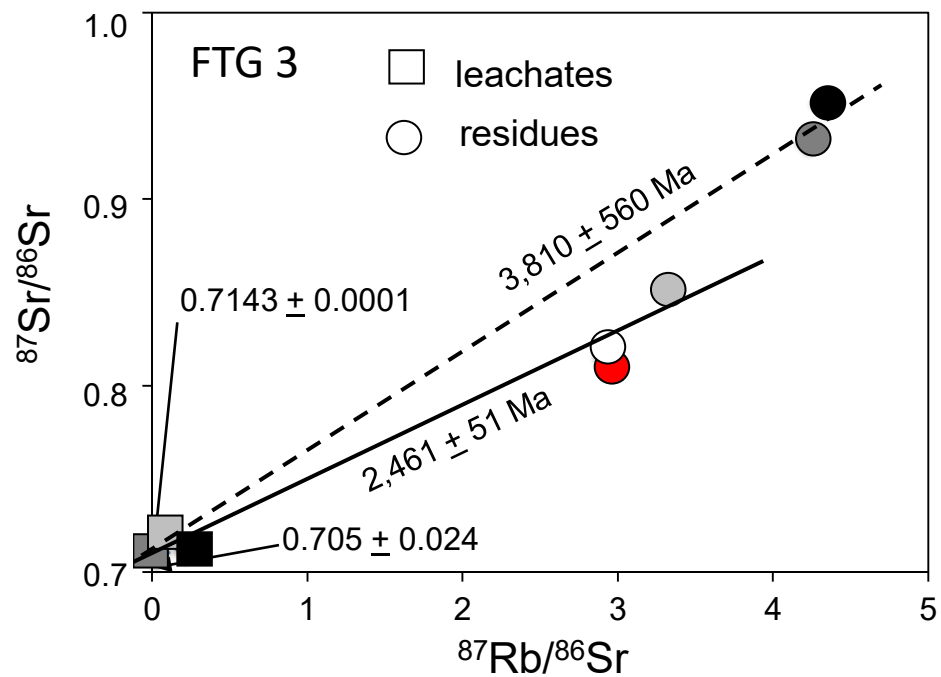
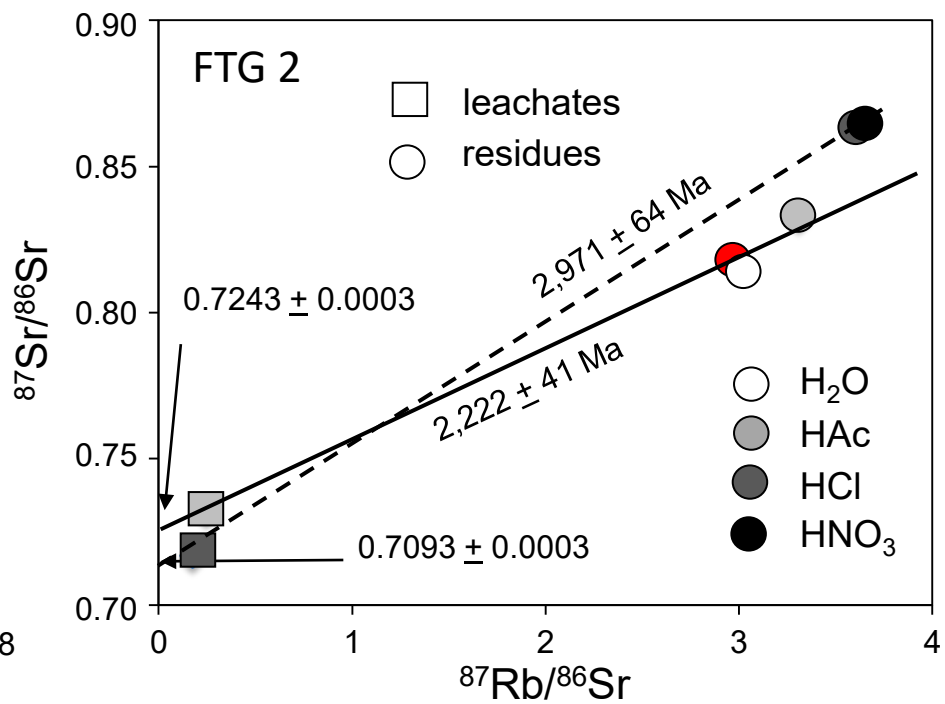
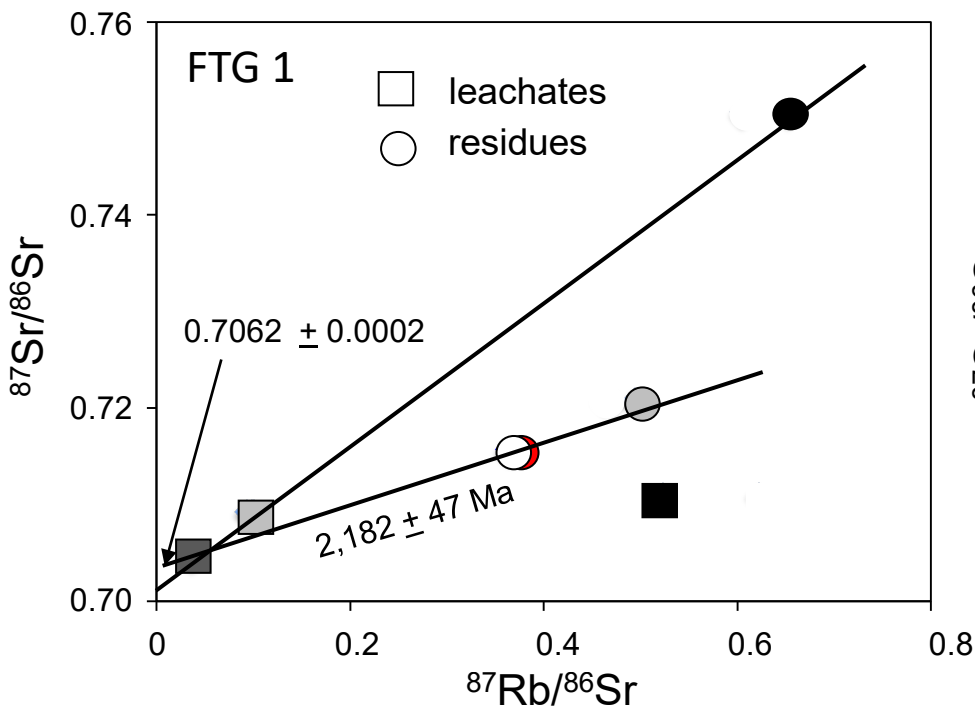


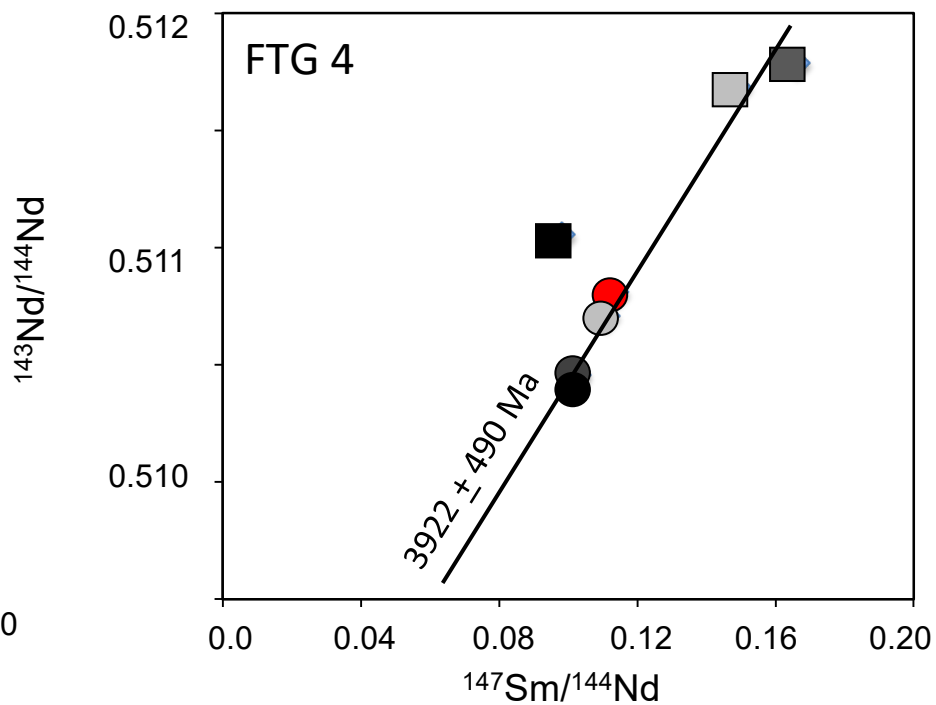
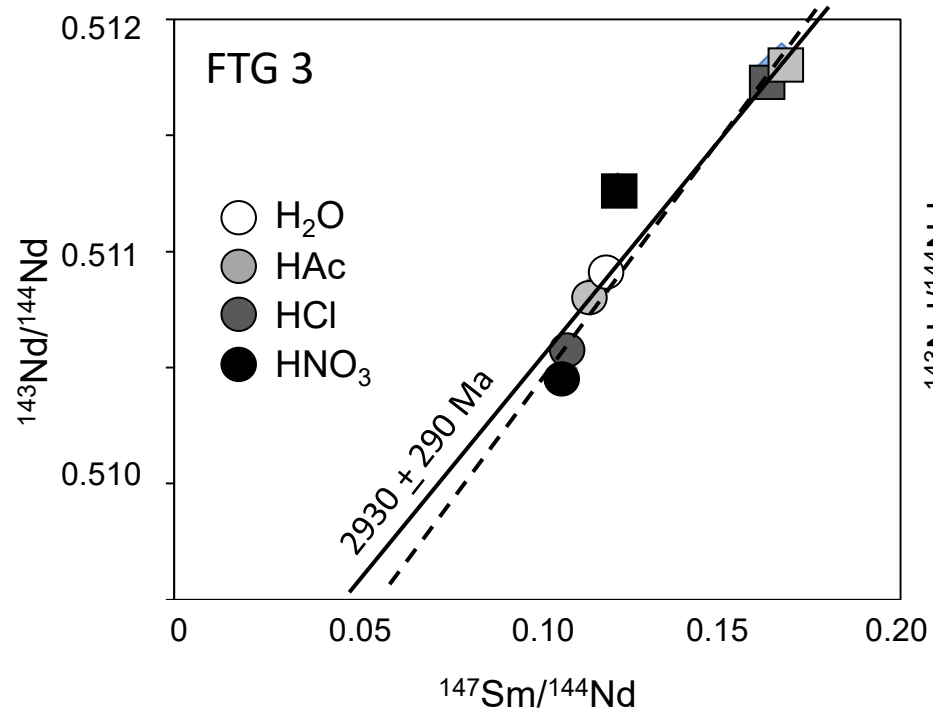
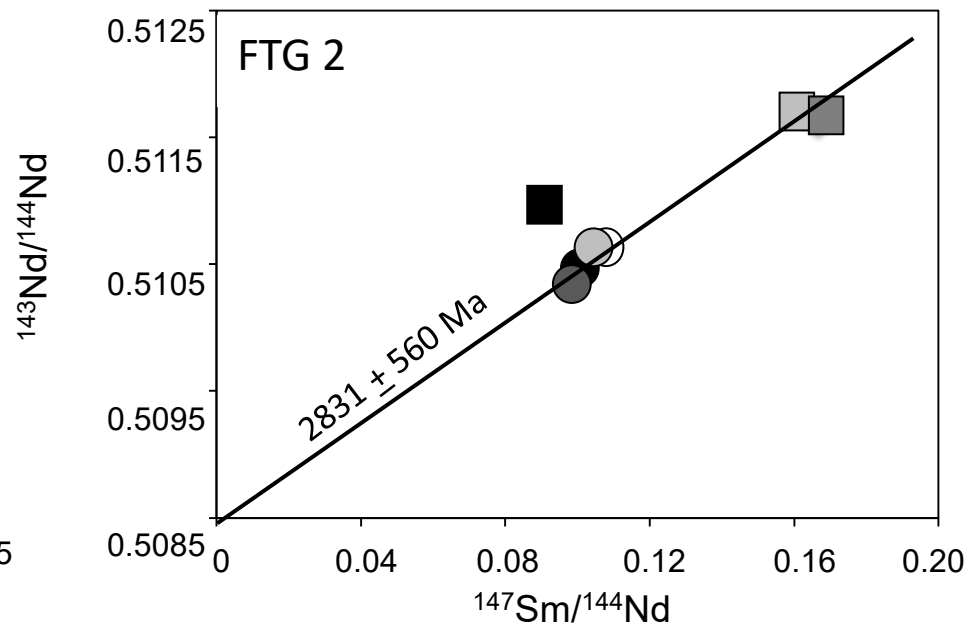
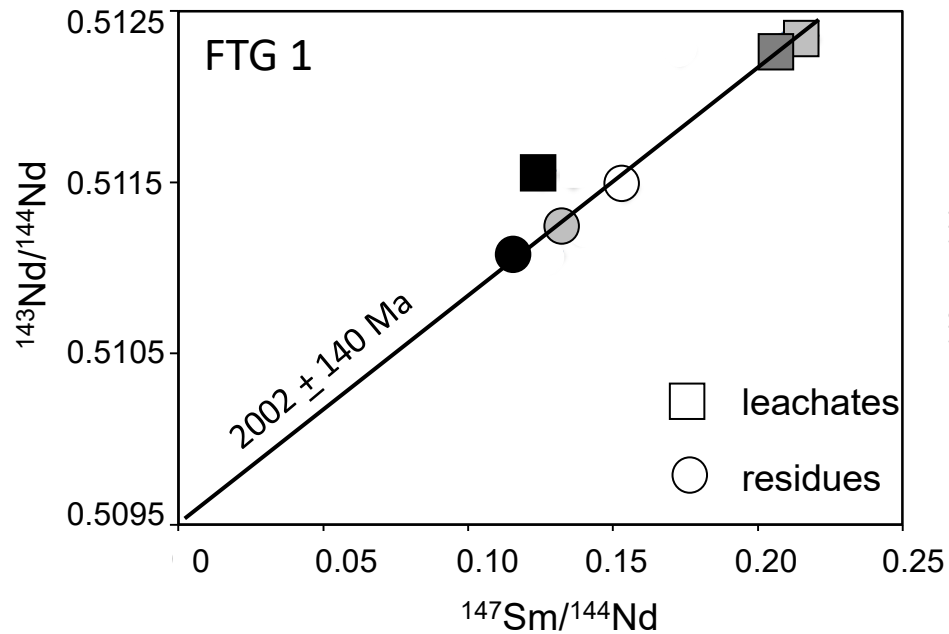


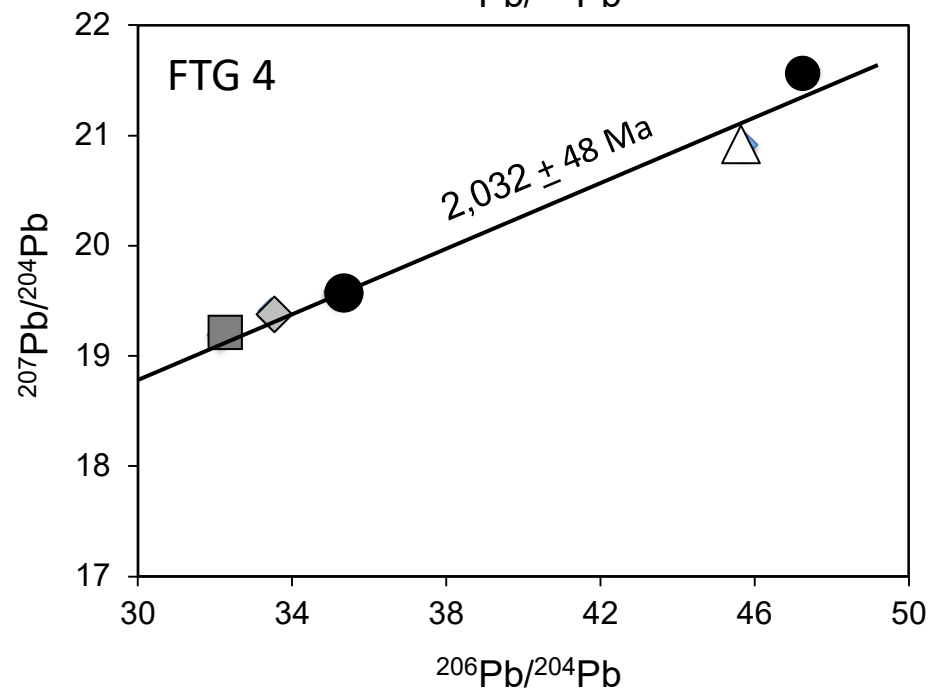
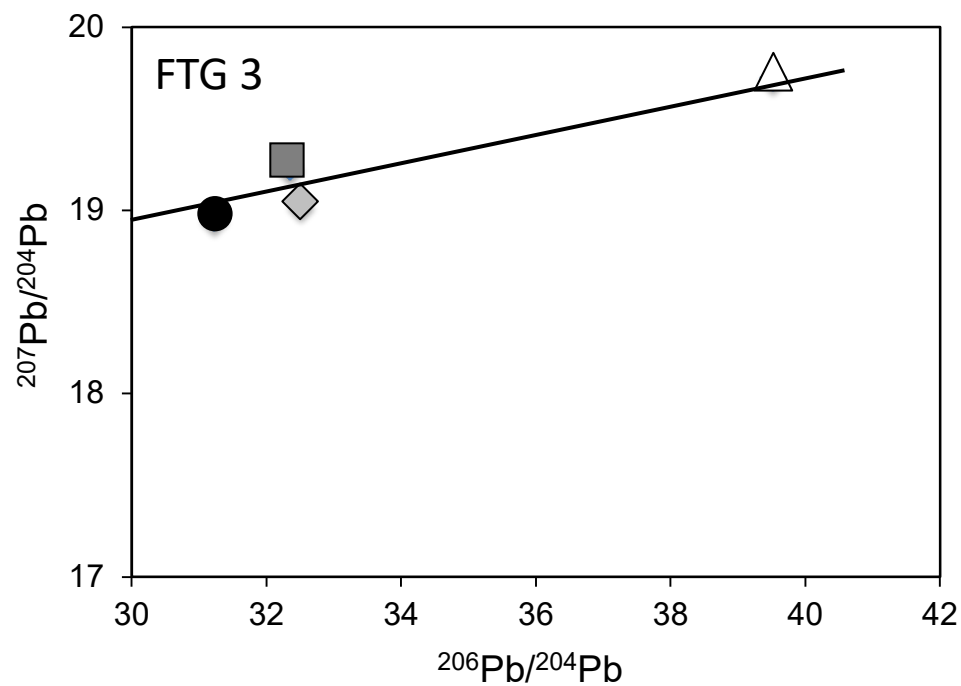
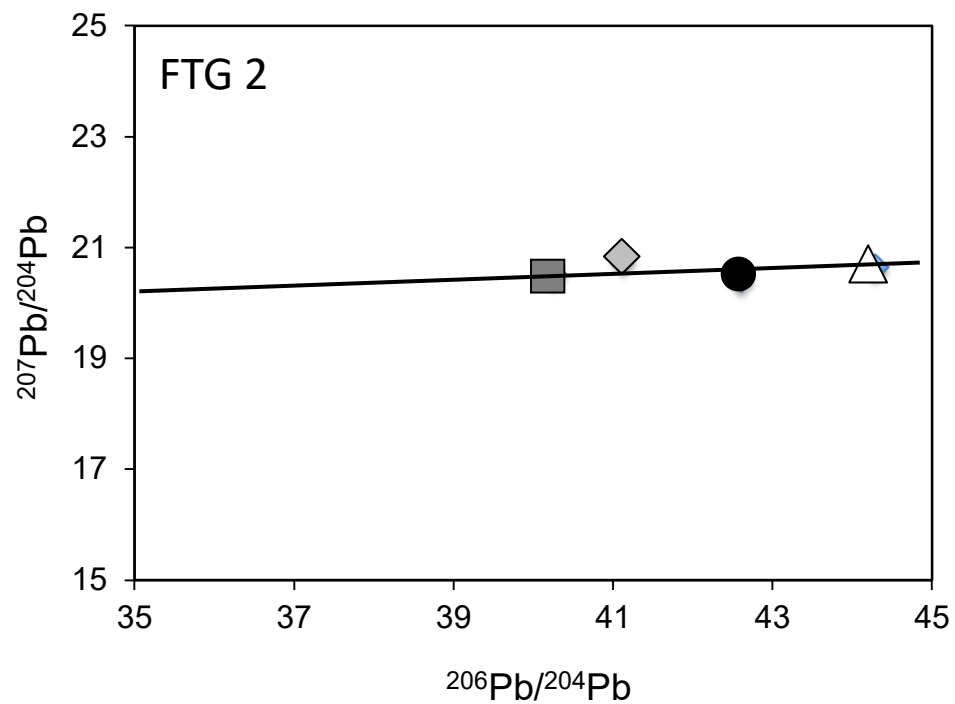
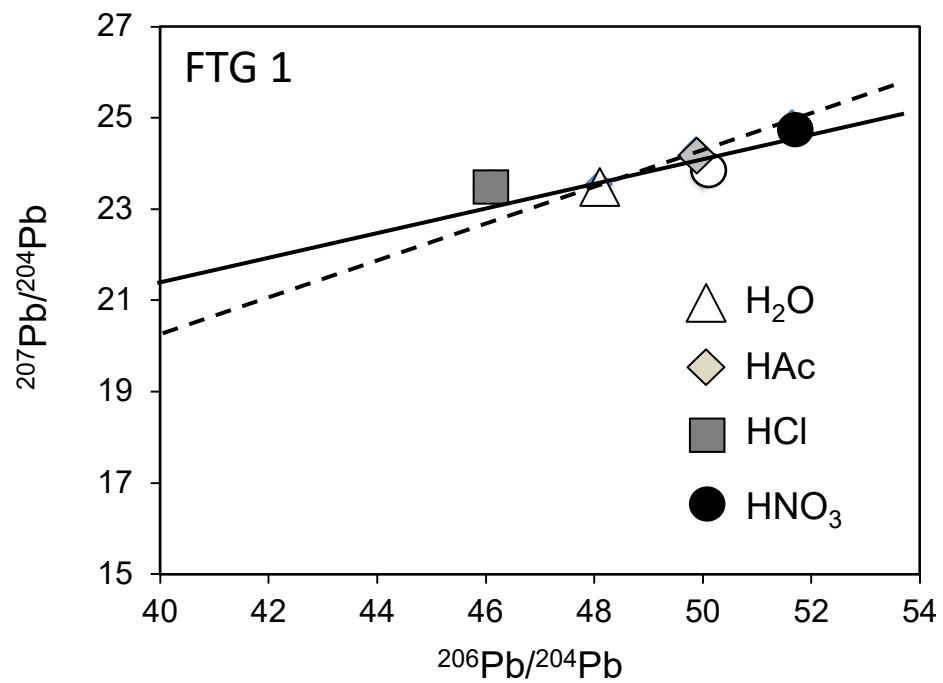


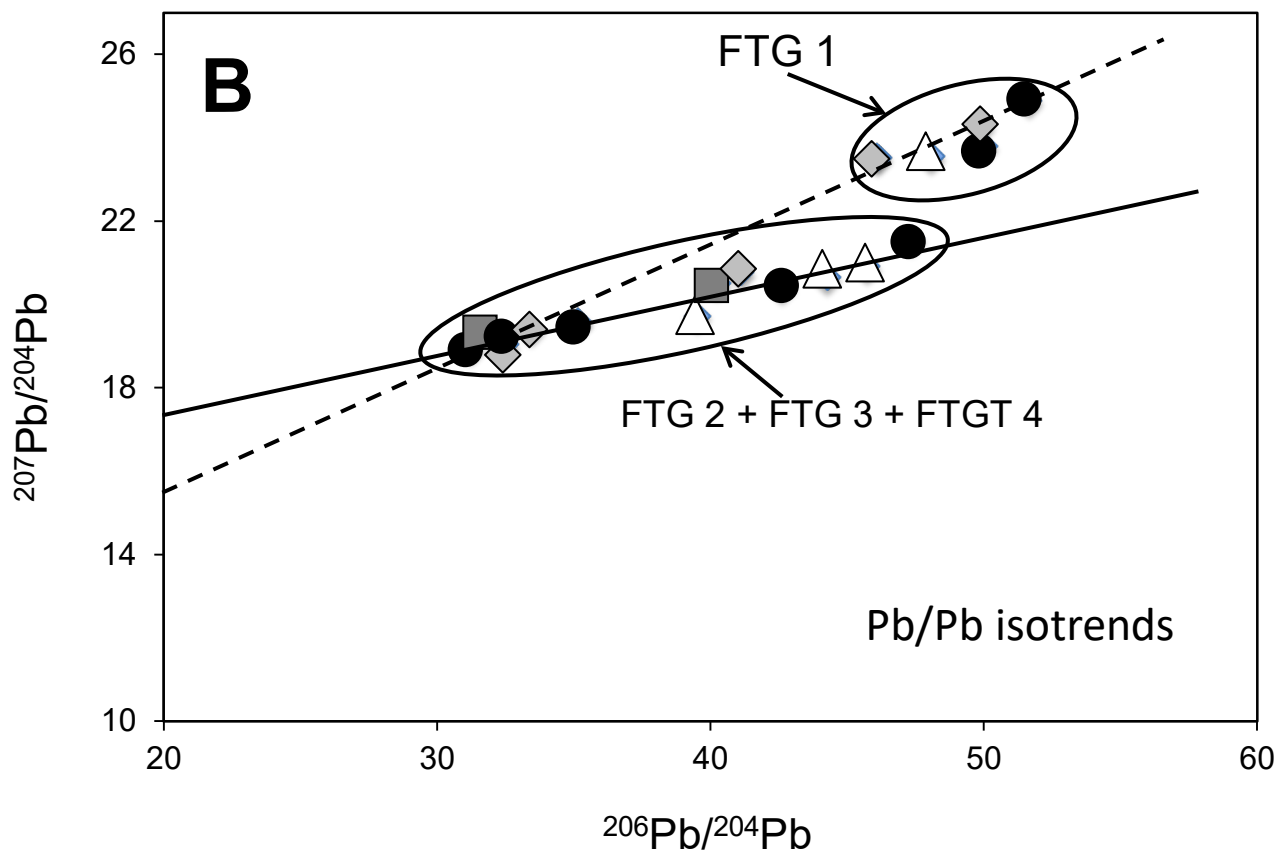
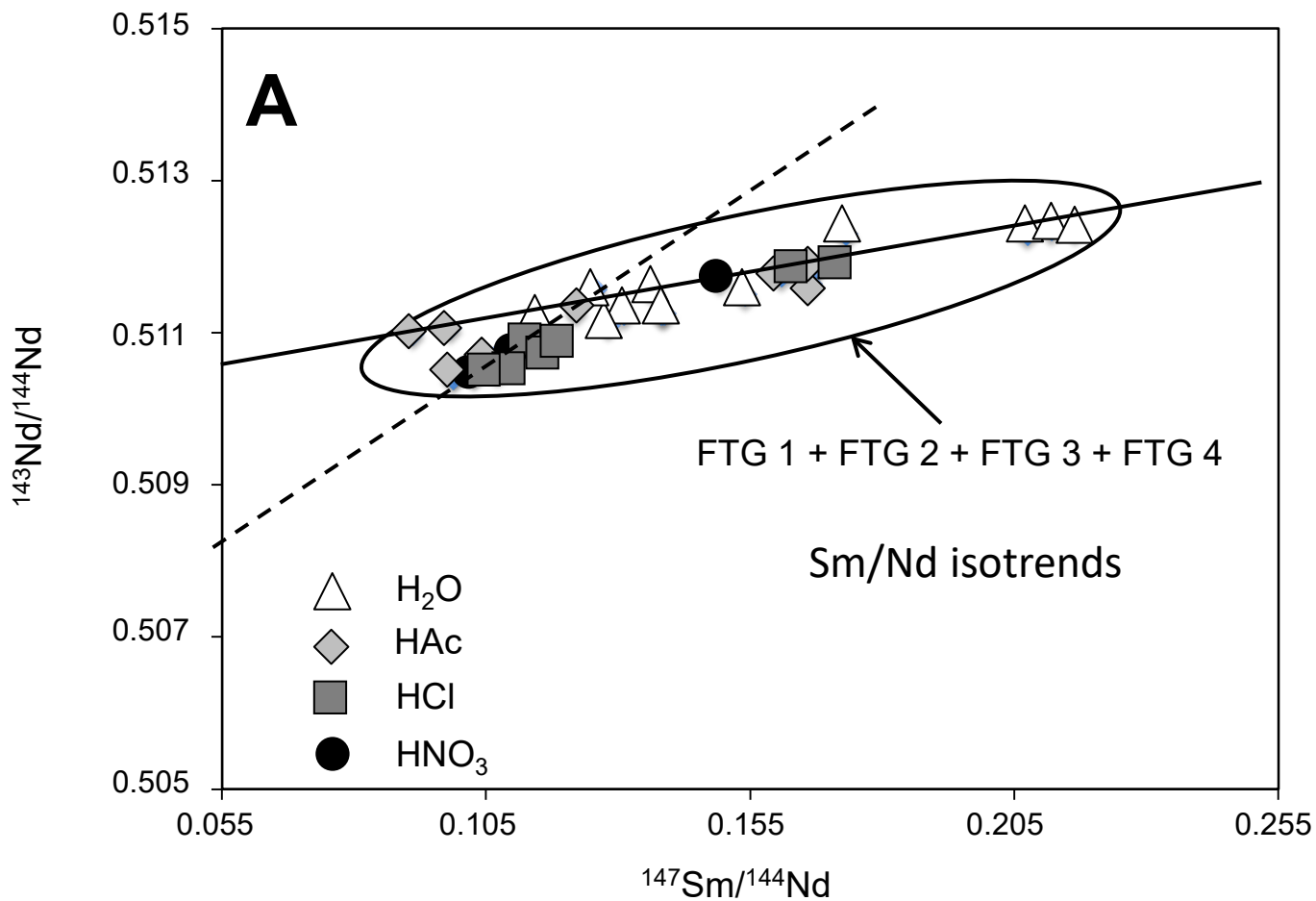


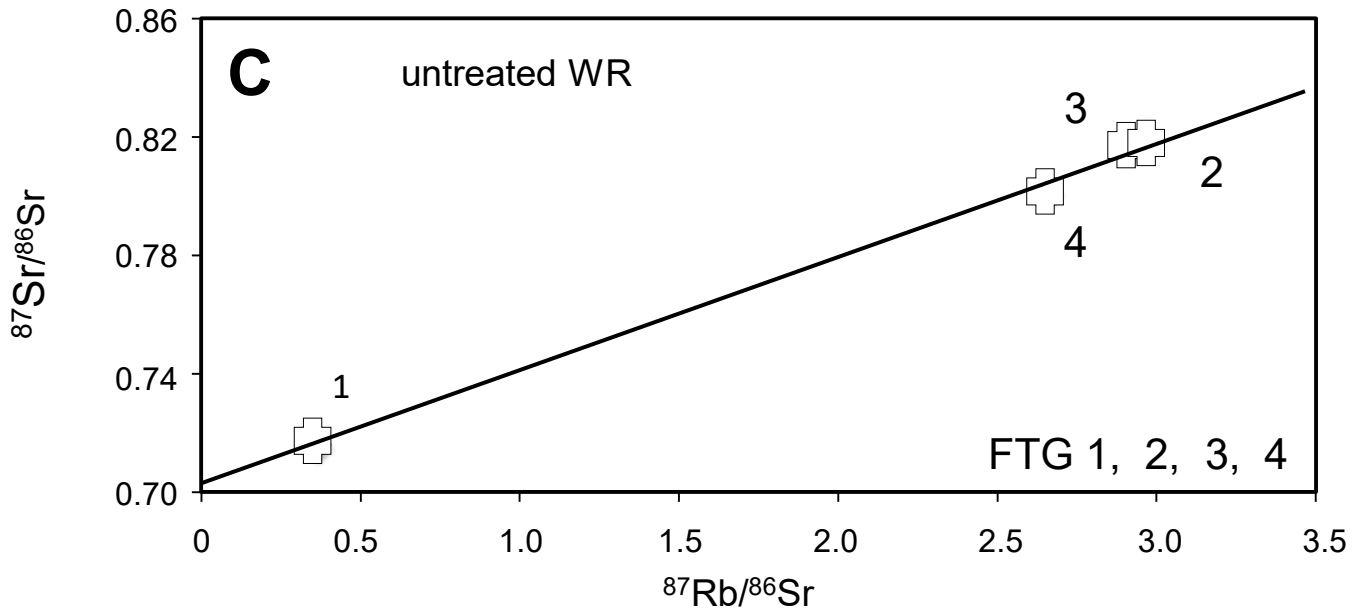
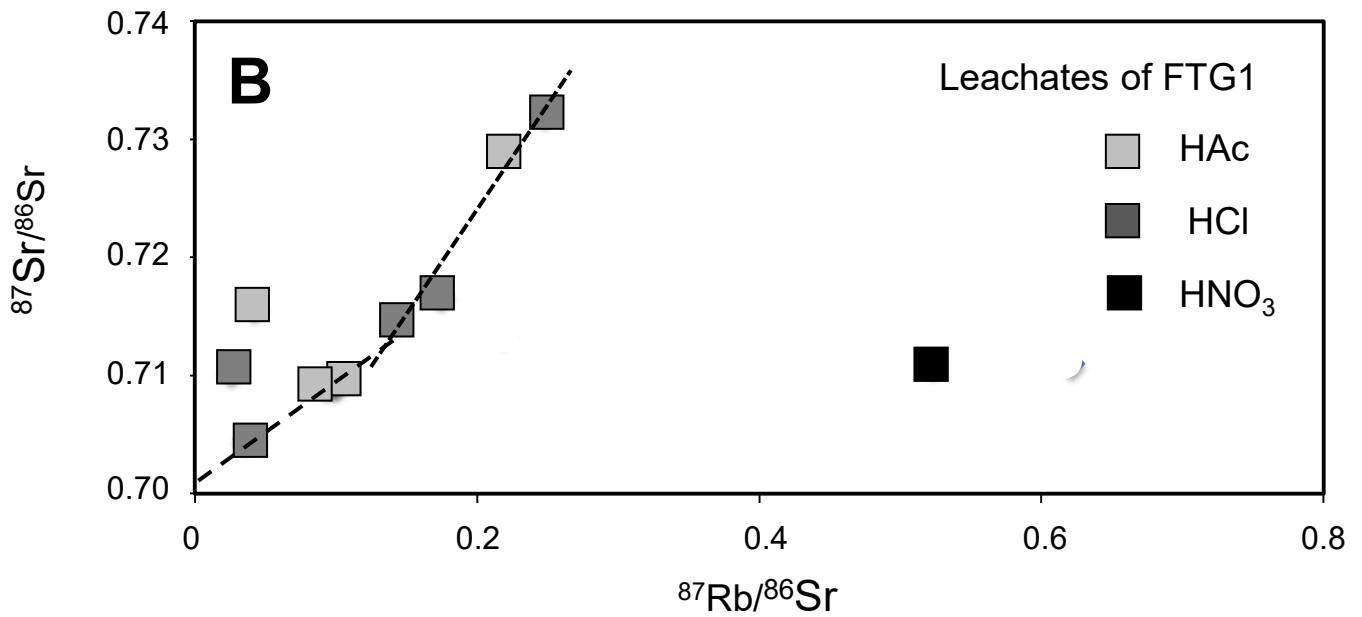
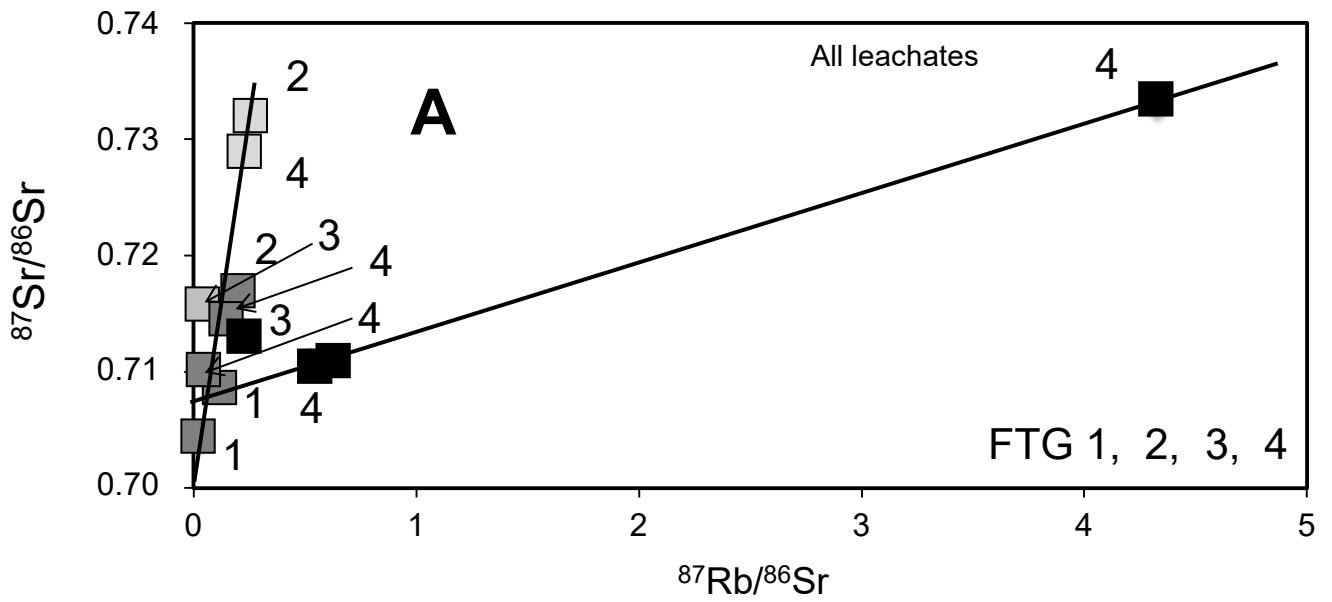


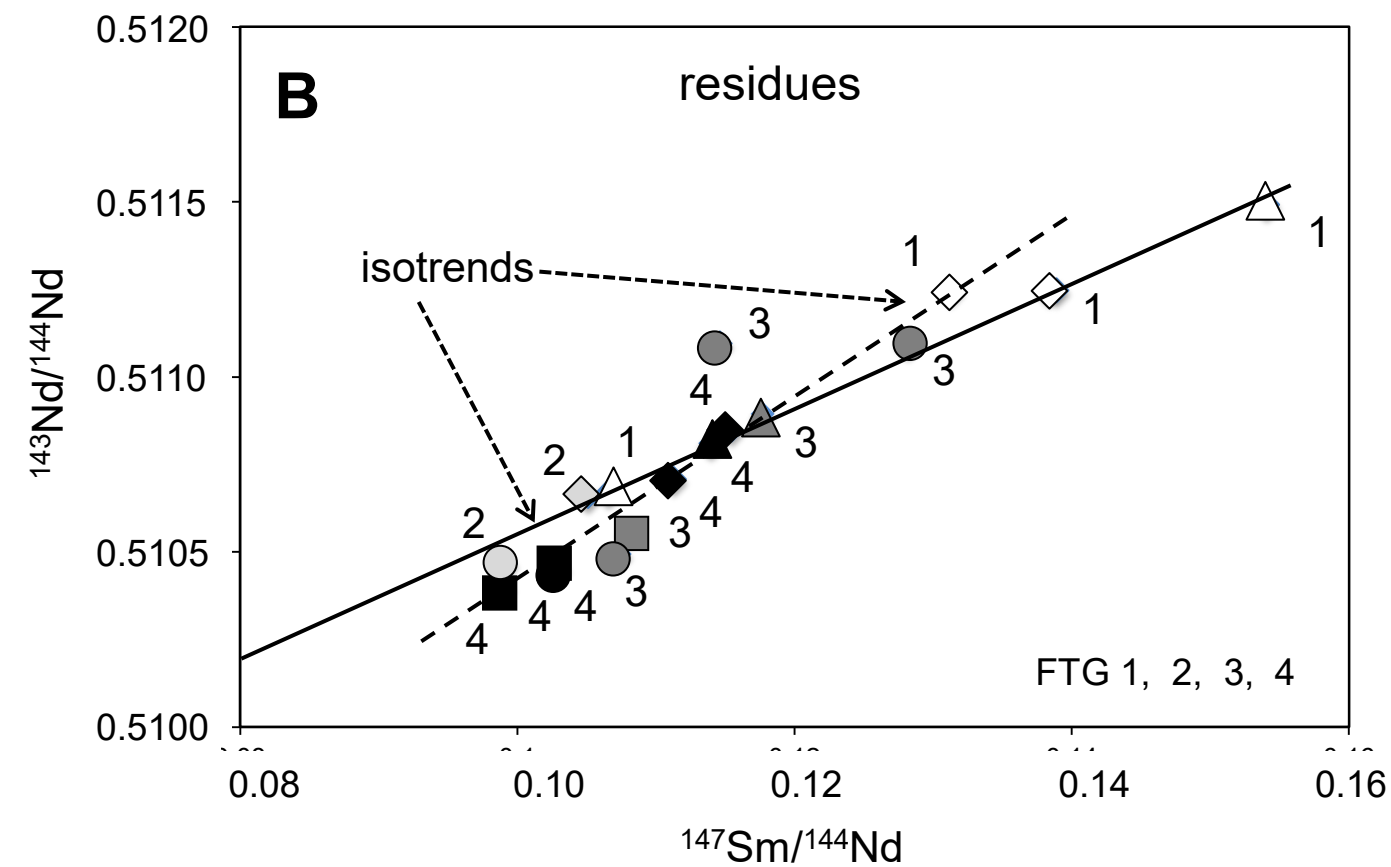
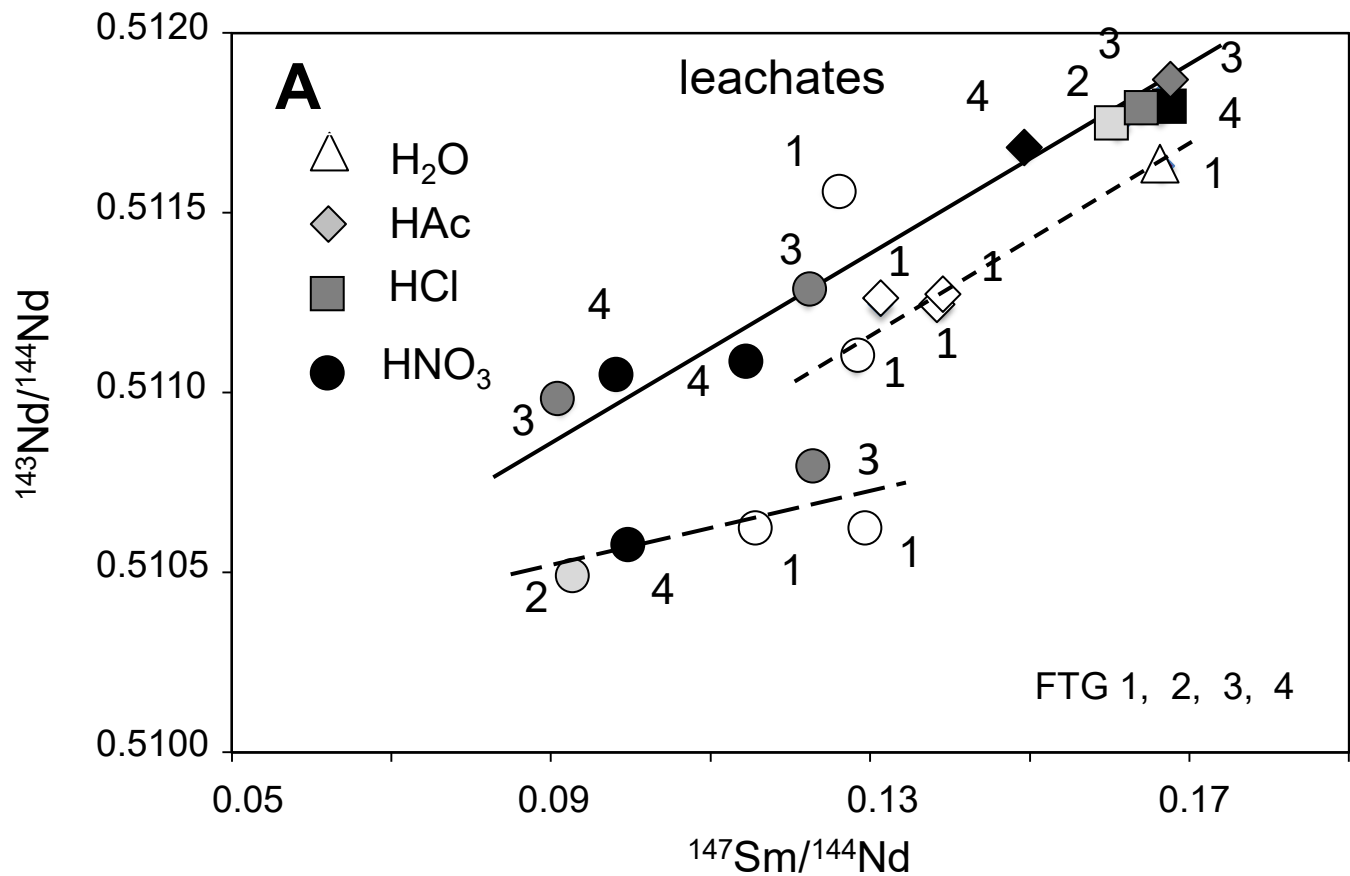


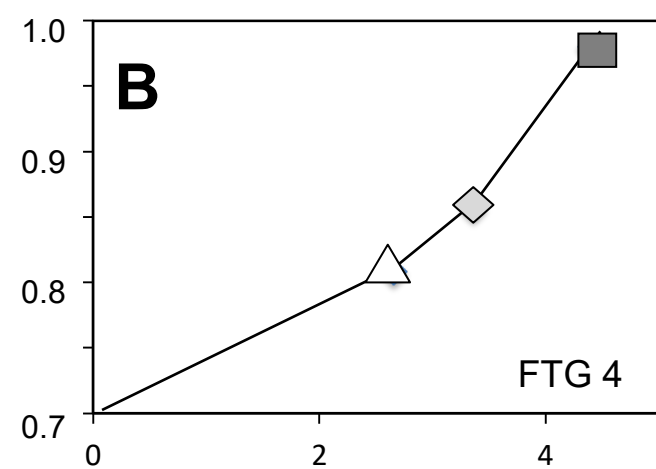
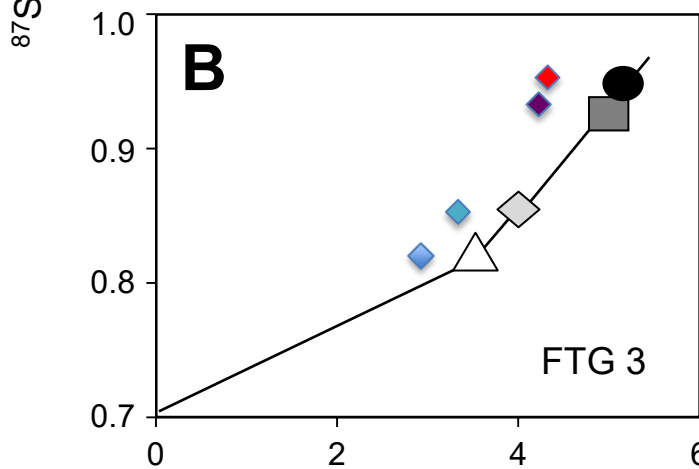
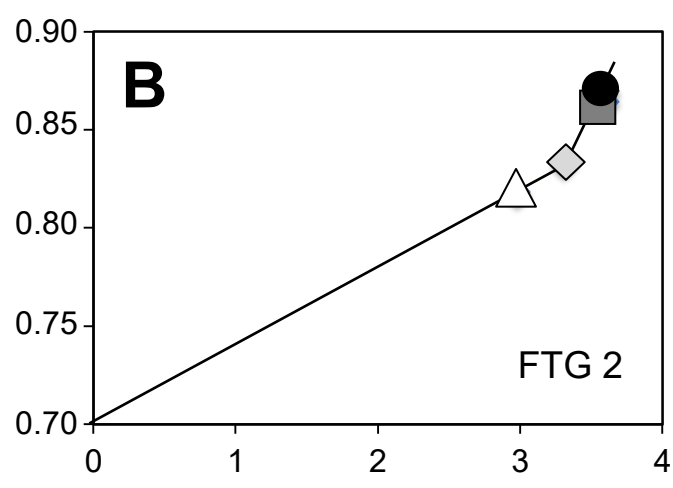
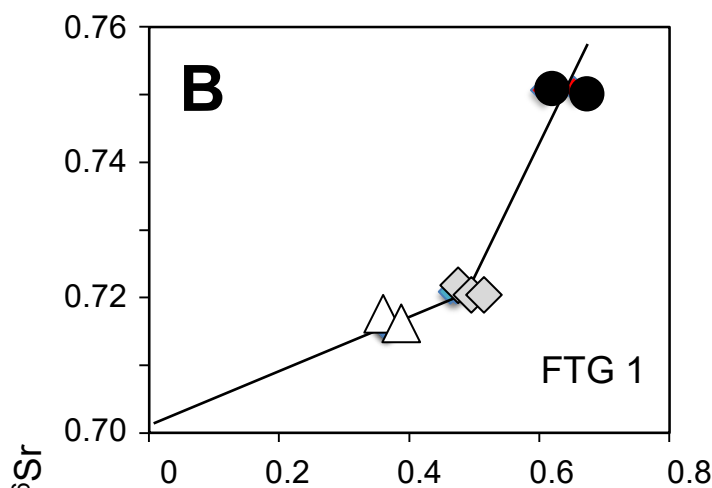
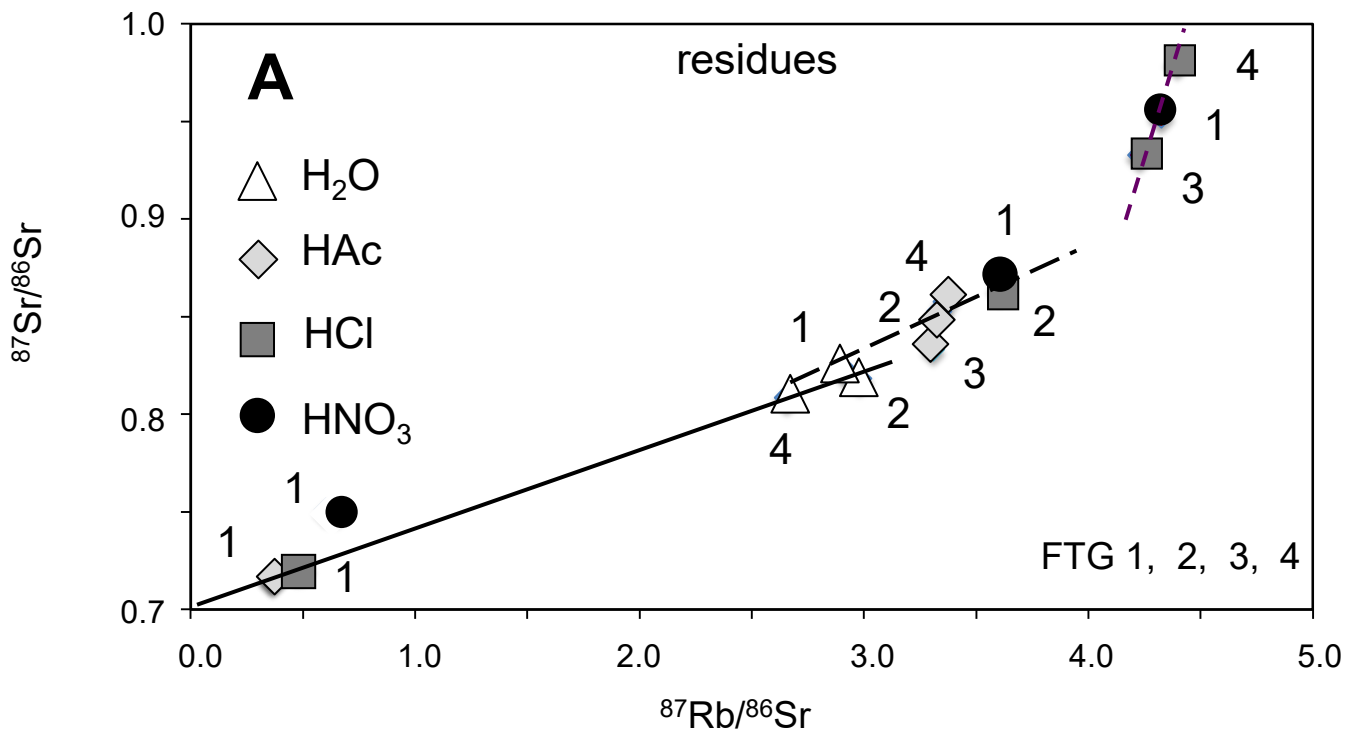














| Sample IDs | removed by H <sub>2</sub> O (%) | left after H <sub>2</sub> O leaching (%) | removed by HAc (%) | left after HAc leaching (%) | removed by HCl (%) | left after HCl leaching (%) | removed by HNO <sub>3</sub> (%) | left after HNO <sub>3</sub> leaching (%) | total removed (%) |
|------------|---------------------------------|--|--------------------|-----------------------------|--------------------|-----------------------------|---------------------------------|--|-------------------|
| FTG1       | 0.25                            | 99.78                                    | 28.74              | 71.04                       | nd                 | nd                          | nd                              | nd                                       | nd                |
| FTG1a      | 0.12                            | 99.98                                    | 22.44              | 77.44                       | 31.48              | 45.96                       | 0.46                            | 45.50                                    | 54.50             |
| FTG1b      | 0.24                            | 99.76                                    | 23.82              | 75.93                       | 30.06              | 45.87                       | 1.16                            | 44.71                                    | 55.30             |
| FTG2       | 0.42                            | 99.58                                    | 7.18               | 92.41                       | 8.90               | 83.51                       | 1.14                            | 82.36                                    | 17.64             |
| FTG3       | 0.26                            | 99.74                                    | 5.80               | 93.94                       | 11.97              | 81.97                       | 2.86                            | 79.11                                    | 20.89             |
| FTG4       | 0.40                            | 99.60                                    | 12.09              | 87.51                       | 11.99              | 75.52                       | 0.55                            | 74.97                                    | 25.04             |

nd stands for not determined

| Sample IDs         | Al/Si | Mg/Si | Ca/Si | Fe/Si | Mn/Si | P/Si | Si/Al | Mg/Al | Ca/Al | Fe/Al | Mn/Al | P/Al | Mg/Ca | Mg/Fe | Ca/Fe | Fe/Mn |
|--------------------|-------|-------|-------|-------|-------|------|-------|-------|-------|-------|-------|------|-------|-------|-------|-------|
| FTG1               |       |       |       |       |       |      |       |       |       |       |       |      |       |       |       |       |
| LH <sub>2</sub> O  | 0.98  | 21.2  | 18.3  | 0.13  | 0.02  | nd   | 1.02  | 21.7  | 18.7  | 0.13  | 0.02  | nd   | 1.16  | 168   | 145   | 6.54  |
| LaH <sub>2</sub> O | 0.33  | 12.7  | 13.2  | 0.04  | 0.03  | nd   | 3.00  | 38.2  | 39.6  | 0.13  | 0.09  | nd   | 0.96  | 292   | 303   | 1.45  |
| LaHAc              | 1.50  | 25.0  | 48.9  | 13.0  | 1.74  | nd   | 0.67  | 16.7  | 32.6  | 8.68  | 1.16  | nd   | 0.51  | 1.92  | 3.75  | 7.48  |
| LaHCl              | 1.49  | 28.9  | 50.4  | 16.3  | 1.76  | 0.12 | 0.67  | 19.4  | 33.9  | 10.9  | 1.18  | 0.08 | 0.57  | 1.78  | 3.10  | 9.22  |
| LaHNO <sub>3</sub> | 1.10  | 2.54  | 5.67  | 1.43  | 0.21  | nd   | 0.91  | 2.31  | 5.17  | 1.31  | 0.19  | nd   | 0.45  | 1.77  | 3.95  | 6.81  |
| LbH <sub>2</sub> O | 0.30  | 12.7  | 15.0  | 0.03  | 0.04  | nd   | 3.31  | 42.0  | 49.7  | 0.11  | 0.13  | nd   | 0.84  | 397   | 470   | 0.79  |
| FTG2               |       |       |       |       |       |      |       |       |       |       |       |      |       |       |       |       |
| LH <sub>2</sub> O  | 0.21  | 2.06  | 5.64  | 0.01  | 0.01  | nd   | 4.85  | 10.0  | 27.4  | 0.05  | 0.05  | nd   | 0.37  | 200   | 547   | 1.00  |
| LHAc               | 1.55  | 7.16  | 15.8  | 7.68  | 0.54  | nd   | 0.65  | 4.62  | 10.2  | 4.96  | 0.35  | nd   | 0.45  | 0.93  | 2.05  | 14.1  |
| LHCl               | 1.70  | 6.76  | 14.5  | 7.53  | 0.38  | 0.52 | 0.59  | 3.99  | 8.56  | 4.44  | 0.23  | 0.31 | 0.47  | 0.90  | 1.93  | 19.6  |
| LHNO <sub>3</sub>  | 4.22  | 3.46  | 5.30  | 9.45  | 0.17  | nd   | 0.24  | 0.82  | 1.26  | 2.24  | 0.04  | nd   | 0.65  | 0.37  | 0.56  | 55.4  |
| FTG3               |       |       |       |       |       |      |       |       |       |       |       |      |       |       |       |       |
| LH <sub>2</sub> O  | 0.06  | 1.97  | 6.68  | 0.00  | 0.01  | nd   | 16.0  | 31.5  | 107   | 0.08  | 0.12  | nd   | 0.29  | 410   | 1390  | 0.67  |
| LHAc               | 2.73  | 45.9  | 121   | 55.2  | 4.48  | nd   | 0.37  | 16.8  | 44.4  | 20.2  | 1.64  | nd   | 0.38  | 0.83  | 2.20  | 12.3  |
| LHCl               | 1.31  | 32.7  | 75.6  | 39.4  | 2.29  | 0.85 | 0.76  | 24.9  | 57.6  | 30.0  | 1.74  | 0.65 | 0.43  | 0.83  | 1.92  | 17.2  |
| LHNO <sub>3</sub>  | 0.84  | 16.0  | 37.2  | 19.1  | 1.35  | nd   | 1.19  | 19.2  | 44.4  | 22.9  | 1.61  | nd   | 0.43  | 0.84  | 1.94  | 14.2  |
| FTG4               |       |       |       |       |       |      |       |       |       |       |       |      |       |       |       |       |
| LH <sub>2</sub> O  | 0.29  | 1.86  | 4.90  | 0.01  | 0.00  | nd   | 3.42  | 6.35  | 16.7  | 0.03  | 0.01  | nd   | 0.38  | 217   | 573   | 2.80  |
| LHAc               | 2.18  | 11.0  | 26.7  | 13.8  | 0.92  | nd   | 0.46  | 5.04  | 12.3  | 6.33  | 0.42  | nd   | 0.41  | 0.80  | 1.94  | 15.0  |
| LHCl               | 1.58  | 6.50  | 14.5  | 8.17  | 0.48  | 0.20 | 0.63  | 4.11  | 9.19  | 5.17  | 0.30  | 0.13 | 0.45  | 0.80  | 1.78  | 17.0  |
| LHNO <sub>3</sub>  | 3.01  | 0.73  | 0.64  | 1.61  | 0.07  | nd   | 0.33  | 0.24  | 0.21  | 0.53  | 0.02  | nd   | 1.14  | 0.45  | 0.40  | 24.4  |

nd stands for not determined

| Sample IDs                             | $\Sigma$ REE<br>( $\mu\text{g/g}$ ) | $\Delta$ REE after<br>leaching ( $\mu\text{g/g}$ ) | $\Delta$ REE after leaching<br>and before next step |
|--|-------------------------------------|--|---|
| <b>FTG1</b>                            |                                     |  |   |
| WR                                     | 24.04                               |  |   |
| HAc leachate                           | 25.04                               | + 1.00   | + 1.00  |
| HAc <sub>a</sub> leachate              | 24.05                               | + 0.10   | + 0.10  |
| HAc <sub>b</sub> leachate              | 24.04                               | 0  | 0   |
| HCl leachate                           | 19.00                               | - 5.04   | - 5.04  |
| HCl <sub>b</sub> leachate              | 19.32                               | - 4.72   | - 4.72  |
| HNO <sub>3</sub> <sub>a</sub> leachate | 14.25                               | - 9.79   | - 5.07  |
| HNO <sub>3</sub> <sub>b</sub> leachate | 15.27                               | - 8.79   | - 4.07  |
| <b>FTG2</b>                            |                                     |  |   |
| WR                                     | 133.3                               |  |   |
| HAc leachate                           | 133.2                               | - 0.1  | - 0.1   |
| HCl leachate                           | 129.6                               | - 3.70   | - 3.60  |
| HNO <sub>3</sub> leachate              | 119.4                               | - 13.9   | - 10.1  |
| <b>FTG3</b>                            |                                     |  |   |
| WR                                     | 58.23                               |  |   |
| HAc leachate                           | 58.25                               | 0  | 0   |
| HCl leachate                           | 55.89                               | - 2.34   | - 2.36  |
| HNO <sub>3</sub> leachate              | 49.49                               | - 8.74   | - 5.40  |
| <b>FTG4</b>                            |                                     |  |   |
| WR                                     | 67.61                               |  |   |
| HAc leachate                           | 67.61                               | 0  | 0   |
| HCl leachate                           | 62.65                               | - 4.94   | - 4.94  |
| HNO <sub>3</sub> leachate              | 54.65                               | - 12.96  | - 7.98  |

The successive leaching steps are H<sub>2</sub>O, HAc, HCl and HNO<sub>3</sub>,  $\Sigma$  □□□□□□ for □ total amounts and  $\Delta$  for the difference with previous step



| Sample IDs         | $^{87}\text{Rb}/^{86}\text{Sr}$ | $\Delta$ duplicates<br>( $\pm 2\sigma$ ) | $^{87}\text{Sr}/^{86}\text{Sr}$ | $^{147}\text{Sm}/^{144}\text{Nd}$ | $\Delta$ duplicates<br>( $\pm 2\sigma$ ) | $^{143}\text{Nd}/^{144}\text{Nd}$ |
|--------------------|---------------------------------|--|---------------------------------|-----------------------------------|--|-----------------------------------|
| FTG1               |                                 |  |                                 |                                   |  |                                   |
| WR                 | 0.3691                          |  | 0.715911                        |                                   |  |                                   |
| RH <sub>2</sub> O  | 0.3620                          |  | 0.715755                        | 0.1541                            |  | 0.5114924                         |
| RaH <sub>2</sub> O | 0.3656                          | $\pm 0.5\%$                              |                                 |                                   |  |                                   |
| RbH <sub>2</sub> O | 0.3660                          | $\pm 0.6\%$                              |                                 |                                   |  |                                   |
| LHAc               | 0.0932                          |  | 0.709280                        |                                   |  |                                   |
| LaHAc              | 0.0981                          | $\pm 2.6\%$                              |                                 | 0.2121                            |  | 0.5123555                         |
| LbHAc              | 0.1007                          | $\pm 2.3\%$                              |                                 | 0.2165                            | $\pm 1.1\%$                              |                                   |
| RHAc               | 0.4935                          |  | 0.720857                        | 0.1313                            |  | 0.5112473                         |
| RaHAc              | 0.4715                          | $\pm 2.3\%$                              |                                 | 0.1389                            | $\pm 2.9\%$                              |                                   |
| RbHAc              | 0.4630                          | $\pm 3.1\%$                              |                                 | 0.1384                            | $\pm 2.7\%$                              |                                   |
| LaHCl              | 0.0362                          |  | 0.704651                        | 0.2076                            |  | 0.5122928                         |
| LbHCl              |                                 |  |                                 | 0.1733                            | $\pm 8.3\%$                              |                                   |
| LaHNO <sub>3</sub> | 0.5231                          |  | 0.711000                        | 0.1257                            |  | 0.5115660                         |
| LbHNO <sub>3</sub> | 0.6221                          | $\pm 9.0\%$                              |                                 | 0.1363                            | $\pm 4.2\%$                              |                                   |
| RHNO <sub>3</sub>  | 0.6524                          |  | 0.750623                        | 0.1146                            |  | 0.5110959                         |
| RaHNO <sub>3</sub> | 0.6048                          | $\pm 3.7\%$                              |                                 | 0.1282                            | $\pm 6.0\%$                              |                                   |
| FTG2               |                                 |  |                                 |                                   |  |                                   |
| WR                 | 2.9784                          |  | 0.818820                        |                                   |  |                                   |
| RH <sub>2</sub> O  | 2.9776                          |  | 0.818141                        | 0.1066                            |  | 0.5106722                         |
| LHAc               | 0.2482                          |  | 0.732237                        | 0.1610                            |  | 0.5117447                         |
| RHAc               | 3.3071                          |  | 0.832956                        | 0.1051                            |  | 0.5106597                         |
| LHCl               | 0.1748                          |  | 0.716810                        | 0.1666                            |  | 0.5116317                         |
| RHCl               | 3.6048                          |  | 0.864351                        | 0.0989                            |  | 0.5103987                         |
| LHNO <sub>3</sub>  |                                 |  |                                 | 0.0912                            |  | 0.5109811                         |
| RHNO <sub>3</sub>  | 3.6072                          |  | 0.864967                        | 0.0991                            |  | 0.5104668                         |
| FTG3               |                                 |  |                                 |                                   |  |                                   |
| WR                 | 2.9242                          |  | 0.816945                        |                                   |  |                                   |
| RH <sub>2</sub> O  | 2.9334                          |  | 0.819994                        | 0.1177                            |  | 0.5108943                         |
| LHAc               | 0.0428                          |  | 0.715848                        | 0.1673                            |  | 0.5118425                         |
| RHAc               | 3.3344                          |  | 0.852722                        | 0.1155                            |  | 0.5108468                         |
| LHCl               | 0.0261                          |  | 0.710414                        | 0.1639                            |  | 0.5117936                         |
| RHCl               | 4.2271                          |  | 0.932831                        | 0.1081                            |  | 0.5105603                         |
| LHNO <sub>3</sub>  | 0.2185                          |  | 0.713684                        | 0.1222                            |  | 0.5112813                         |
| RHNO <sub>3</sub>  | 4.3224                          |  | 0.952914                        | 0.1073                            |  | 0.5104942                         |
| FTG4               |                                 |  |                                 |                                   |  |                                   |
| WR                 | 2.6639                          |  | 0.808146                        |                                   |  |                                   |
| RH <sub>2</sub> O  | 2.6536                          |  | 0.808361                        | 0.1140                            |  | 0.5108097                         |
| LHAc               | 0.2202                          |  | 0.729089                        | 0.1493                            |  | 0.5116862                         |
| RHAc               | 3.3605                          |  | 0.857557                        | 0.1113                            |  | 0.5107080                         |
| LHCl               | 0.1415                          |  | 0.714659                        | 0.1663                            |  | 0.5117872                         |
| RHCl               | 4.3939                          |  | 0.980399                        | 0.1027                            |  | 0.5104699                         |
| LHNO <sub>3</sub>  | 4.3294                          |  | 0.732991                        | 0.0983                            |  | 0.5110541                         |
| RHNO <sub>3</sub>  |                                 |  |                                 | 0.1029                            |  | 0.5104538                         |

| Sample IDs        | $^{206}\text{Pb}/^{204}\text{Pb}$ | ( $\pm 2\sigma$ ) | $^{207}\text{Pb}/^{204}\text{Pb}$ | ( $\pm 2\sigma$ ) |
|-------------------|-----------------------------------|-------------------|-----------------------------------|-------------------|
| FTG1              |                                   |                   |                                   |                   |
| RH <sub>2</sub> O | 48.099                            | 0.015             | 23.542                            | 0.011             |
| LHAc              | 46.156                            | 0.014             | 23.511                            | 0.011             |
| RHAc              | 49.891                            | 0.007             | 24.288                            | 0.003             |
| LHCl              | 46.088                            | 0.014             | 23.556                            | 0.011             |
| LHNO <sub>3</sub> | 50.018                            | 0.016             | 23.794                            | 0.011             |
| RHNO <sub>3</sub> | 51.650                            | 0.001             | 24.891                            | 0.001             |
| FTG2              |                                   |                   |                                   |                   |
| RH <sub>2</sub> O | 44.291                            | 0.014             | 20.643                            | 0.009             |
| LHAc              | 41.128                            | 0.013             | 20.776                            | 0.009             |
| LHCl              | 40.257                            | 0.013             | 20.508                            | 0.009             |
| LHNO <sub>3</sub> | 42.610                            | 0.013             | 20.417                            | 0.009             |
| FTG3              |                                   |                   |                                   |                   |
| RH <sub>2</sub> O | 39.524                            | 0.012             | 19.723                            | 0.009             |
| LHAc              | 32.513                            | 0.010             | 19.032                            | 0.009             |
| LHCl              | 32.355                            | 0.010             | 19.234                            | 0.009             |
| LHNO <sub>3</sub> | 31.230                            | 0.010             | 18.957                            | 0.009             |
| FTG4              |                                   |                   |                                   |                   |
| RH <sub>2</sub> O | 45.731                            | 0.014             | 20.911                            | 0.010             |
| LHAc              | 33.460                            | 0.010             | 19.408                            | 0.009             |
| LHCl              | 32.142                            | 0.010             | 19.189                            | 0.009             |
| LHNO <sub>3</sub> | 35.163                            | 0.011             | 19.582                            | 0.009             |
| RHNO <sub>3</sub> | 47.365                            | 0.018             | 21.588                            | 0.008             |

| Sample IDs | Rb-Sr (1)          | Rb-Sr (2)          | Sm-Nd (1)    | Sm-Nd (2)    | Pb-Pb (1)            | Pb-Pb (2)            |
|------------|--------------------|--------------------|--------------|--------------|----------------------|----------------------|
| FTG 1      | <b>2182 +/- 47</b> |                    | 2002 +/- 140 |              |                      |                      |
| FTG 2      | <b>2971 +/- 64</b> | <b>2222 +/- 41</b> | 2831 +/- 560 |              | 2800 +/- 260 (leach) |                      |
| FTG 3      | <b>2461 +/- 51</b> |                    | 2930 +/- 290 | 3343 +/- 440 | 2850 +/- 760 (leach) |                      |
| FTG 4      | 2824 +/- 87        |                    | 3922 +/- 490 | 1444 +/- 180 | <b>2032 +/- 48</b>   | 2749 +/- 490 (leach) |