

## AUTHIGENIC TI-BEARING CRYSTALS IN A PRECAMBRIAN CLAY FROM BUENOS AIRES PROVINCE, ARGENTINA

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**Abstract**—The Precambrian Villa Mónica Formation clay was analyzed using petrographic and scanning electron microscopy, X-ray diffraction and chemical analysis, with the aim of characterizing the Ti-bearing phases present and determining their possible origin and/or source. Two Ti-bearing minerals were found to be present, rutile and anatase. The crystals are needles between 5 and 15  $\mu\text{m}$  in size, with no evidence of abrasion or corrosion. They are commonly found in association with the (001) faces of illite flakes or in the pores between the flakes. Their disposition is similar in the three quarries studied. No zonation or differential settling due to differences in specific gravity was observed. In addition, chemical analyses indicated a positive correlation between  $\text{TiO}_2$  and  $\text{K}_2\text{O}$  suggesting that both oxides behave similarly after the deposition of the sediment. The  $\text{TiO}_2$  content in the bulk fraction ranges from 0.8 to 1.98 wt.%, values that are similar to those exhibited in other clay deposits from different ages and geneses.

All observations are consistent with an *in situ* origin of these Ti-bearing phases during post-depositional processes that included recrystallization of existing minerals and crystallization of new phases. The original detrital minerals such as biotite, ilmenite as well as detrital illite, were the primary sources of the  $\text{TiO}_2$  and of the Fe oxides that coat the clay. Understanding the origin and the reaction mechanisms involved during the post-depositional alteration of the Villa Mónica Formation suggests that the Ti-bearing phases in different sediment types were formed by similar mechanisms involving redox processes at low to medium temperatures, even in Precambrian sediments where the presence of rutile could lead to an incorrect assumption of high temperatures involved.

**Key Words**—Anatase, Compositional Data, Illite, Precambrian Clay, Rutile, SEM, X-ray Diffraction.

### INTRODUCTION

Titanium occurs as free oxides and as structural  $\text{Ti}^{4+}$  in silicates. Much of the Ti in the finer-particle size fractions of sedimentary rocks ( $<20 \mu\text{m}$ ) occurs in secondary minerals derived from *in situ* alteration of primary Fe-Ti oxide minerals such as ilmenite ( $\text{FeTiO}_3$ ) (Schroeder *et al.*, 2002; Grey and Reid, 1975). In the coarse-silt and fine-sand fractions the Ti resides in primary minerals such as rutile and brookite ( $\text{TiO}_2$ ), sphene ( $\text{CaSiTiO}_6$ ) and ilmenite ( $\text{FeTiO}_3$ ).

Ti-bearing phases have been reported in fireclays, ballclays and kaolin deposits from all over the world (Nagelschmidt *et al.*, 1949; Konta and Borovec, 1966; Sayin and Jackson, 1975; Schroeder and Shiflet, 2000) occurring primarily as needles and/or pseudomorphic crystals of anatase and rutile. These Ti-bearing phases were reported to be detrital grains or, alternatively, they are thought to have been derived from the *in situ* alteration of detrital Fe-Ti oxide grains. In addition, metamorphic, hydrothermal and diagenetic processes have been mentioned as possible processes playing a part in their crystallization (Morad and Aldahan, 1982; Valentine and Commeau, 1990).

The purpose of this paper is to document the mineralogy and possible origin of Ti-bearing needles

in an Argentinian Precambrian illitic clay using optical petrography, electron microscopy, energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and chemical analysis.

### GEOLOGICAL SETTING

The study area is located in the Sierras Septentrionales hills of east central Argentina (Figure 1). Precambrian granitic basement rocks underlying five marine Upper Precambrian to Lower Paleozoic sedimentary sequences are exposed in outcrops. The sediments are mainly siliciclastics along with some carbonate rock facies such as dolostone and limestone.

The clay that was studied belongs to the first sequence, the Villa Mónica Formation (Poiré, 1987), which occurs directly above the Precambrian basement and is Neoproterozoic in age (800 m.y.) (Iñiguez *et al.*, 1989). The sequence starts with a quartzite followed by the clay layer that can be traced laterally into a dolostone facies. The second sedimentary sequence begins with a new quartzitic layer above the clay.

The clay bed is 7–10 m thick and ranges from massive to bedded (Figure 2). It comprises illite, quartz and Fe oxides (hematite and goethite) and is characteristically pale to dark yellow in color. Light green lenses up to 10 cm thick and several meters long are interbedded. The mineralogical composition of these lenses is similar to the yellow clay, except for the absence of Fe oxides and the presence of weathered

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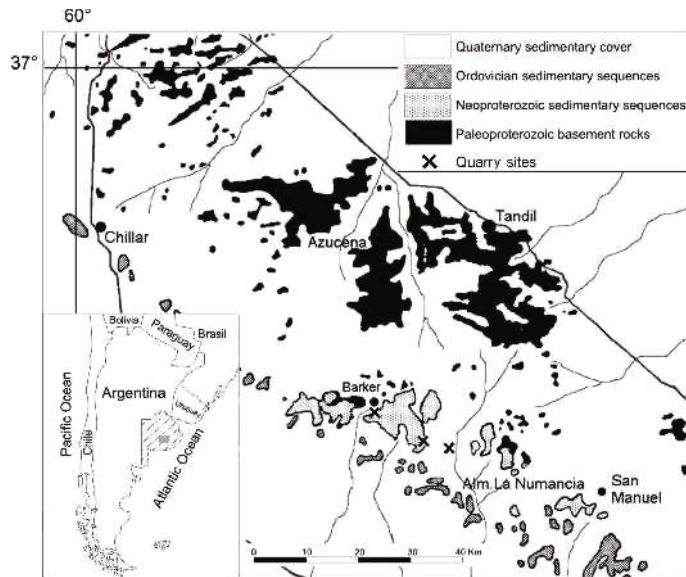


Figure 1. Geological and location map of the study area.

pyrite crystals. Previous studies on illite crystallinity standard index, polytypes and quartz fluid inclusions have shown that the clay was subjected to temperature and pressure conditions of deep diagenesis *i.e.* very low-grade metamorphism (Alló *et al.*, 1996; Alló and Domínguez, 2002).

The Precambrian basement of the area is composed mainly of granitic, migmatitic and metamorphic rocks. The  $\text{TiO}_2$  content ranges from 0.35 to 1.29% in low-grade metamorphic rocks (Teruggi *et al.*, 1988) and between 0.58 and 0.61% in basic dikes (Teruggi *et al.*, 1974). All these rocks were eroded during transgressive processes and subsequently modified by weathering.

## MATERIALS AND METHODS

The samples were taken from three quarries east and southeast of Barker, in Buenos Aires province (Figure 1).

Thin-sections were prepared and examined using petrographic microscopy at magnifications of 5 to 100 times.

Particle morphology and texture were observed by scanning electron microscopy (SEM) using a JEOL JSM 35 CF microscope, with 60 Å resolution, a secondary electron detector and an EDAX energy dispersive spectral X-ray detector.

A portion of each sample was disaggregated and the 2–20 µm fraction was separated by settling and centrifugation methods. Powder XRD analyses were conducted on the >2 µm, 2–20 µm and >20 µm fractions using a Rigaku Geiger Flex Mac III diffractometer, operating at 35 kV and 25 mA with  $\text{CuK}\alpha$  radiation with a graphite monochromator and computerized data-collection system. The sample preparations were randomly oriented and a  $2^\circ/2\theta/\text{min}$  scanning speed was used.

Whole-rock chemical analyses were performed by inductively coupled plasma emission spectrometry (Actlabs, Ancaster, Canada). The data were analyzed using the Aitchison transformation for compositional data (Aitchison, 1986). This method was used in order to minimize the constant sum effect. As a result, the study of chemical data by this method is concerned with the relative magnitudes of the ingredients rather than their absolute values. Aitchison (1986) proposed that the compositional data be expressed as covariances of log-ratios of the variables rather than raw percentages. Thus, the calculation of log-ratios has the consequence of freeing sample values from a restricted range where they always have to reach 100% to vary between  $\pm$  infinity. The datasets are also spread during the transformation to allow differences to be more easily distinguished.

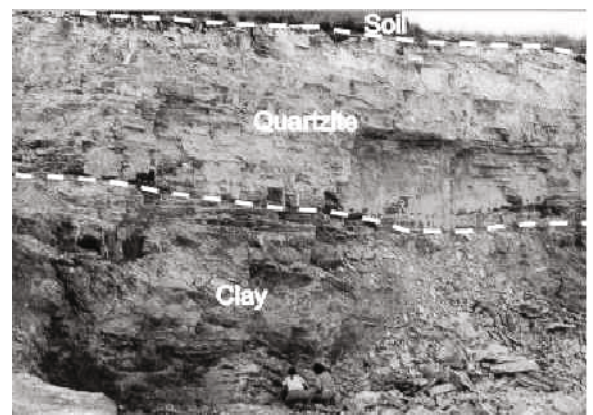


Figure 2. Outcrop view of the Villa Mónica Formation clay and upper quartzitic layer and soil.

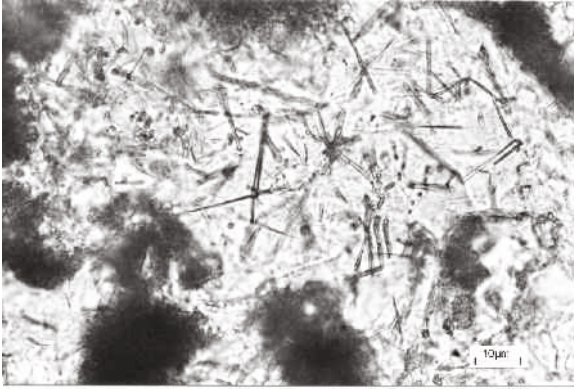


Figure 3. Photomicrograph of the Villa Mónica clay showing acicular Ti-bearing crystals distributed randomly over the illitic matrix.

## RESULTS

Ti-bearing crystals were observed in both the yellow clay and the green clay lenses, which represent a restricted anoxic environment in the Precambrian Villa Mónica formation (Alló, 2001).

Anatase and rutile crystals show an acicular habit, with some occurring as twinned crystals (Figure 3). They are 5–15  $\mu\text{m}$  in size and display a reddish-brown to greenish-blue color under polarized light. Due to their small crystal size ( $<15 \mu\text{m}$ ), interference figures could not be used to optically distinguish rutile from anatase. Figure 3 displays a random distribution of the Ti-bearing crystals representative of all the samples collected from the three quarries.

The SEM images in Figure 4 of acicular crystals show no evidence of mechanical abrasion or chemical dissolution. The Ti-bearing crystals are not only located within the pore spaces between illite flakes but also appear on the basal (001) surfaces of the illite. The EDAX spectra corroborate the  $\text{TiO}_2$  composition of the crystals (Figure 5).

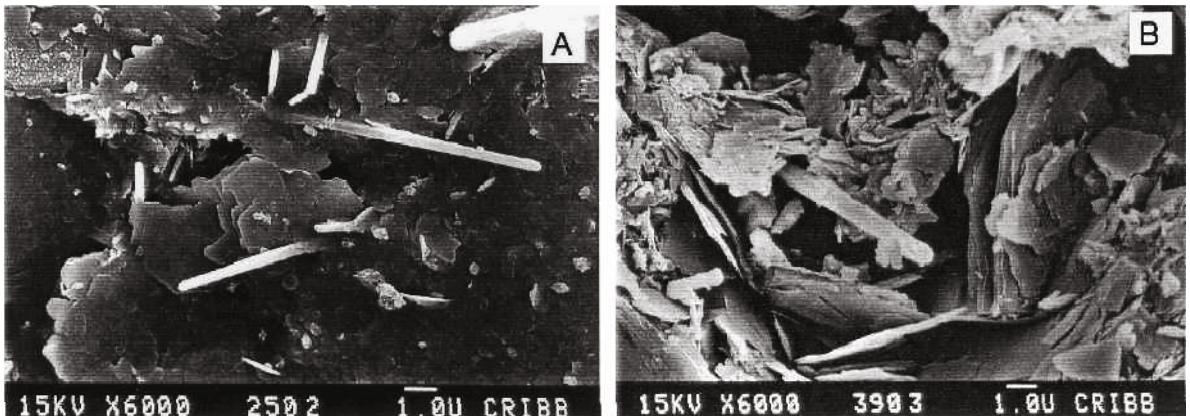


Figure 4. SEM images: (a) Ti-bearing crystals on the illite flake surfaces; (b) Ti-bearing crystals in a pore between illite flakes.

The XRD analyses of the 2–20  $\mu\text{m}$  fraction from the three quarries show a similar pattern revealing along with illite, quartz and Fe oxide minerals, reflections of rutile and anatase. The rutile and anatase reflections are not very strong but are clear and sharp enough to be identified (Figure 6).

The chemical analyses of the bulk material indicate 0.8–1.98 wt.%  $\text{TiO}_2$  content (Table 1). The Aitchinson transformation of the chemical data to compositional data demonstrated a correlation among the sub-composition  $\text{K}_2\text{O}-\text{TiO}_2-\text{Fe}_2\text{O}_3$ , and a clear positive relationship between  $\text{K}_2\text{O}$  and  $\text{TiO}_2$ . Also, a less well defined correlation is shown by the sub-composition  $\text{K}_2\text{O}-\text{TiO}_2-\text{SiO}_2$ .

In Figure 7 the sub-composition  $\text{K}_2\text{O}-\text{TiO}_2-\text{Fe}_2\text{O}_3$  plotted in the ‘simplex’ (Aitchison’s terminology for ‘restricted region’) is shown. After the centered log-ratio transformation (Figure 8), the subcomposition  $\text{K}_2\text{O}-\text{TiO}_2-\text{Fe}_2\text{O}_3$  shows a good relation, which, after the additive log-ratio transformation, reflects positive correlation between  $\text{TiO}_2$  and  $\text{K}_2\text{O}$ . The  $\text{TiO}_2$  is independent of  $\text{Fe}_2\text{O}_3$  (Figure 9).

## DISCUSSION

The Ti-bearing phases present in Villa Mónica clay are mainly rutile and anatase. The XRD patterns show clear reflections that identify both minerals (Figure 6).

The origin of the Ti-bearing phases in shale and clay deposits has been related to the provenance of the sediment, while the post-depositional processes (diagenesis, metamorphism, weathering) are important factors in their occurrence (Force, 1991).

Due to the small size of the crystals in the Villa Mónica clay (mainly  $<15 \mu\text{m}$ ), a detrital origin cannot be ruled out, because they could have been transported long distances and deposited without evidence of physical abrasion. In order to analyze this hypothesis, the density of the Ti-bearing minerals vs. non-Ti-bearing minerals

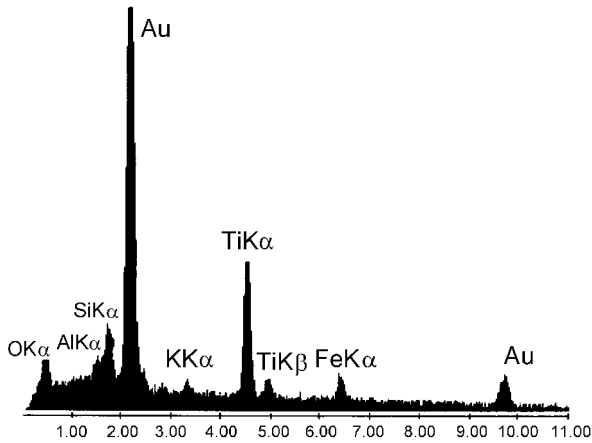


Figure 5. EDAX diagram for an acicular crystal. The Au peaks belong to the coating. Due to the small size and the elongated shape of the crystals, the background was also detected (Al, Si, K from the illite, Fe from the oxides).

must be considered. The density of the Ti-bearing group of minerals (*i.e.* biotite, magnetite, rutile, anatase) ranges from 3.0 to 5.0 g/cm<sup>3</sup> while the density of the non-Ti-bearing group ranges from 2.5 to 3.0 g/cm<sup>3</sup> (Deer *et al.*, 1993). Thus, the density of the Ti-bearing minerals is 0.5 to 2 times greater than the non-Ti-bearing minerals and the hydraulic sorting should have affected the heavy-mineral concentrations in the deposit. Also, size should be considered, and the Ti-bearing crystals are smaller than some of detrital mica flakes, thus the density difference is minimized by the size. Petrographic and electron microscopic observations suggest that no sorting took place and the disposition of the Ti-bearing needles is similar from the bottom to the top in all three quarries.

The Ti-bearing needles present in this clay are intimately associated with the illite flakes, growing in

or on their surfaces, suggesting a possible authigenic origin. Therefore, if any migration of Ti took place it would probably have been from the mica flakes that were dissolved and recrystallized as TiO<sub>2</sub> minerals in the sediment.

Considering that shales and slates from different ages and localities around the world show, on average, 0.49% TiO<sub>2</sub>, with a range of 0 to 1.4% for illites (Weaver, 1989; Berger *et al.*, 1999), the Villa Mónica clay does not display anomalous contents of this oxide. Additionally, TiO<sub>2</sub> values are analogous in the three pits studied and are consistent with the TiO<sub>2</sub> content of the basement rocks. This suggests that the sources of Ti for anatase and rutile were part of the original sediment and were not imported as dissolved ions from surrounding rocks.

The analysis of the compositional data shows a positive correlation between TiO<sub>2</sub> and K<sub>2</sub>O which implies a close relationship between the presence of Ti-bearing minerals and the presence of the K-phyllosilicates. The K<sub>2</sub>O-TiO<sub>2</sub>-SiO<sub>2</sub> sub-composition also showed a weak correlation. One interesting point is that generally it is assumed that concentrations of Ti and Fe are related. However, in this case, the TiO<sub>2</sub> seems to be independent of the Fe<sub>2</sub>O<sub>3</sub> content. The basement rocks, source of the Villa Monica clay, have several Fe-bearing minerals such as augite, hornblende, micas, ilmenite and magnetite, among others. Poiré (1993) pointed out that in the basement regolith the mafic minerals are no longer preserved but both biotite and Fe oxides are important constituents. One can reasonably conclude, that (1) the primary minerals from which the Ti was released probably did not contain Fe in their structure, (2) the Ti was masked by the total Fe content derived from all the Fe-bearing minerals, or (3) Fe has significantly re-mobilized after oxidation by bacterially produced siderophores.

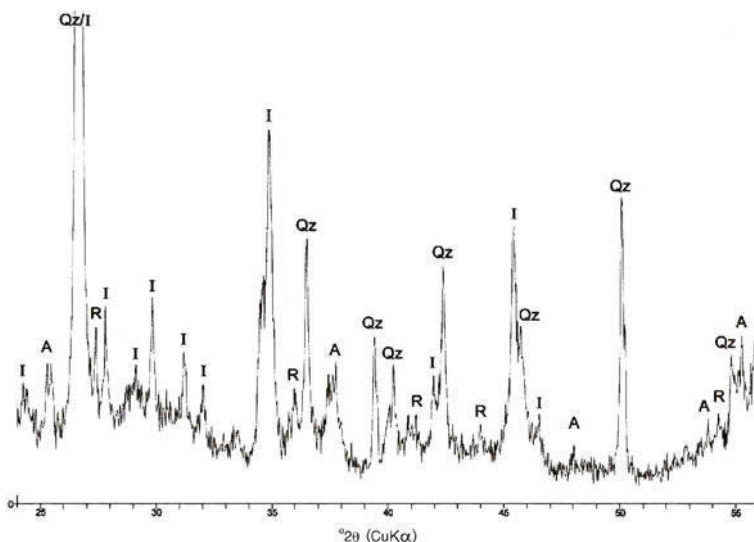


Figure 6. XRD pattern of the fraction between 2 and 20 μm. I: illite, A: anatase, Qz: quartz, R: rutile.

Table 1. Chemical composition of some representative bulk clay samples from the Villa M6nica Formation. The y stands for yellow clay (oxidizing environment) and the g stands for green clay (reducing environment).

Sample	LSV1y	LSV2y	LSV3y	LSV5y	LP12y	LP15y	M27y	M29y	LSV4g	LSV6g	LSV8g	M24g
SiO <sub>2</sub>	44.86	56.08	39.90	44.94	59.51	60.31	47.14	55.06	47.86	57.73	50.04	66.74
Al <sub>2</sub> O <sub>3</sub>	14.13	15.54	14.87	15.77	13.65	18.74	9.48	16.43	29.82	22.38	28.10	17.60
Fe <sub>2</sub> O <sub>3</sub>	26.37	15.90	29.75	24.17	14.71	7.33	31.33	15.66	2.64	3.22	2.61	4.89
MnO	0.25	0.19	0.27	0.82	0.16	0.04	0.21	0.12	0.01	-0.01	0.00	0.00
MgO	1.07	0.76	1.06	0.95	1.03	1.25	0.88	1.50	1.43	1.53	1.69	1.39
CaO	0.20	0.14	0.23	0.29	0.20	0.22	0.32	0.42	0.26	0.30	0.22	0.07
Na <sub>2</sub> O	0.05	0.06	0.11	0.10	0.09	0.09	0.05	0.04	0.07	0.10	0.10	0.04
K <sub>2</sub> O	4.34	3.56	4.30	3.80	4.11	6.10	2.59	5.50	5.38	7.05	9.24	7.17
TiO <sub>2</sub>	0.94	0.83	0.90	0.80	0.82	1.13	0.60	1.06	1.49	1.53	1.98	1.21
P <sub>2</sub> O <sub>5</sub>	0.35	0.17	0.27	0.18	0.30	0.23	0.34	0.29	0.10	0.10	0.07	0.03
L.O.I.	7.43	6.78	8.33	8.17	5.41	4.56	7.06	3.92	10.97	6.07	5.95	0.86
Total	99.99	100.01	99.99	99.99	99.99	100	100	100	100.03	100	100	100

The only K-phyllosilicate present is both detrital and authigenic, so it can be deduced that detrital micas containing Ti in their structure and other Ti-bearing detrital minerals released Ti during the clay recrystallization during the diagenetic process. Morad and Aldahan (1982) reported values of TiO<sub>2</sub> up to 3.8% in biotites from late Precambrian sedimentary rocks in Sweden. They also proposed that the titanium can be released from the biotite structure under low-intensity leaching conditions and oxidized as amorphous matter that then crystallized as one TiO<sub>2</sub> polymorph. Loughnan (1969) proposed a similar mechanism, explaining that the Ti was released as Ti(OH)<sub>4</sub> and when dehydrated precipitated as crystalline TiO<sub>2</sub>. Schroeder *et al.* (2002) also suggested that biotite could have been the precursor of the Fe-Ti-bearing phases in Georgia kaolins, but in that case the amount of biotite seems insufficient to achieve the anatase content in the kaolin.

However, the mineral that has been studied extensively and is likely to be altered to give Ti-bearing new phases is ilmenite. Grey and Reid (1975) and Schroeder *et al.* (2002) proposed a two-step reaction mechanism where the ilmenite is transformed to pseudorutile by a solid-state transformation and later the pseudorutile undergoes incongruent dissolution to form anatase, rutile, hematite and Mn oxides.

In the area of this study, ilmenite was found partly replaced by leucoxene (pseudorutile) in basic dikes of the basement (Teruggi *et al.*, 1974), but biotite is much more abundant (Teruggi and Kilmurray, 1975) and is concentrated in the basement regolith (Poir6, 1993). Consequently, and considering the positive correlation of the TiO<sub>2</sub> with the K<sub>2</sub>O, it is suggested that the primary source of the Ti in these sedimentary rocks may have been biotite. The biotite altered to give illite, anatase, rutile and Fe oxides. A similar two-step mechanism as in the ilmenite could have taken place, with an unstable Ti-

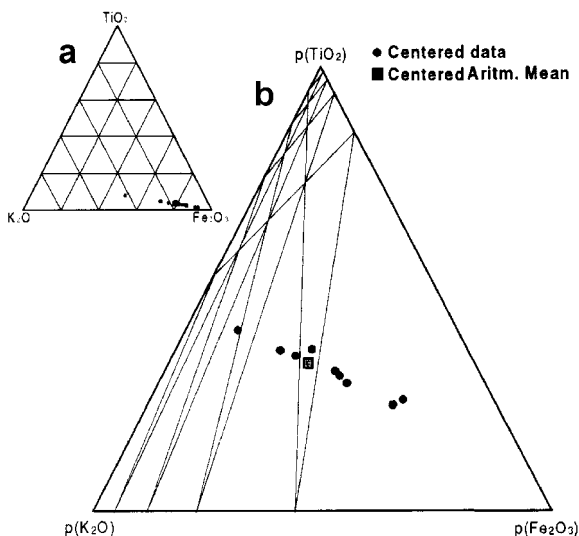


Figure 7. Aitchison's (1986) compositional data transformation. Sub-composition K<sub>2</sub>O-TiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> in the simplex before (a) and after (b) the perturbation and centered.

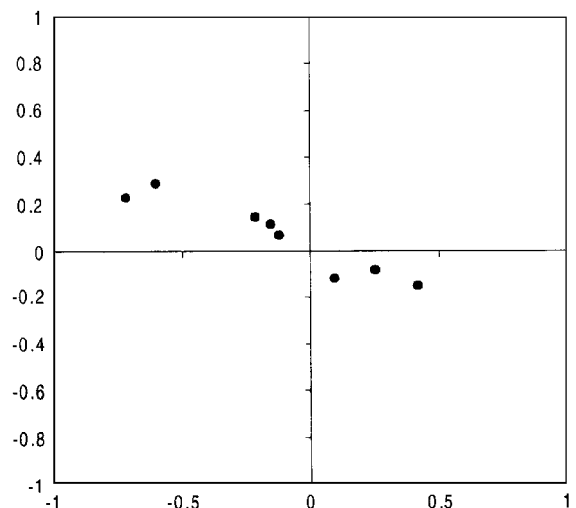


Figure 8. Aitchison's (1986) centered log-ratio transformation of the K<sub>2</sub>O-TiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> sub-composition.

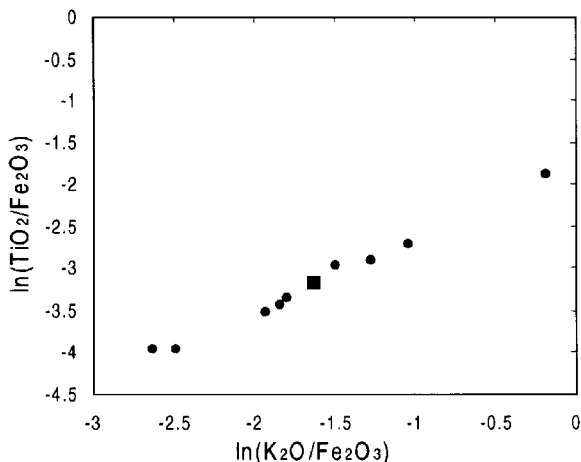


Figure 9. Aitchison's (1986) additive log-transformation. Ratio  $K_2O/Fe_2O_3$  vs.  $TiO_2/Fe_2O_3$ . The dots represent data and the square is the arithmetic mean.

phase forming after the release of the Ti from the biotite structure followed by crystallization of anatase and rutile.

## CONCLUSIONS

Anatase and rutile are the Ti-bearing phases in the Villa Mónica Precambrian clay. They are acicular in habit and range between 5 and 15  $\mu\text{m}$  in size. Their identical distribution from bottom to top of the clay in each of the quarries studied along with the absence of corrosion or dissolution features, the  $TiO_2$ - $K_2O$  positive correlation, and the intimate association with the illite flakes indicate that the rutile crystals grew *in situ* during the post-depositional reorganization of the clay from percolating pore solutions rich in Ti ions. The ions were derived from Ti-bearing detrital minerals such as biotite and ilmenite that were constituents of the basement rocks that were transformed through weathering and diagenesis.

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