PREPARATION OF MULLITE WHISKER FROM POWDER OF PURE TOPAZ AND DOPED RARE EARTH.

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ABSTRACT

Mullite whiskers were obtained by thermal decomposition of powders topaz (Al_2SiO_4 (OH, F)$_2$) pure and doped with 3 and 5 wt% La_2O_3 and Y_2O_3, 1300 and 1400oC, 1h, in air. Both pure mullite whiskers showed how the doped a reason Al_2O_3: SiO_2 close to 2:1, rich in alumina. The aspect ratio (AR) of whiskers varies with the concentration of dopant and temperature treatment. In pure whiskers AR was 28 and 31.5, the 1300 and 1400^{o}C, showing no glassy phase. For whiskers doped, a reduction in AR ranging from 14.13 to 16.10 (3 to 5wt% La_2O_3) and 6.32 to 7.35 (3 to 5wt% Y_2O_3), at 1300 and 1400°C, respectively, and the Y_2O_3 was not entirely incorporated, and a part formed $Y_2Si_2O_7$ and $YO_{1.335}$, according to XRD analysis, presence of small amount of glassy phase.

Keywords: Mullite, topaz, rare earths, whiskers

INTRODUCTION

Whiskers are micrometric monocrystals that have high degree of crystalline perfection, and practically free of defects and therefore mechanical strength close to the theoretical (1). An important feature of whiskers is the aspect ratio - ratio between the length and fiber diameter - very large, ranging from 10 to 100. The whiskers can be

elastically stretched up to 3% without permanent deformation, compared with less than 0.1% for the ceramic body (2). A technological application of whiskers is as a reinforcement element in ceramic composites primarily to prevent crack propagation and improve the mechanical behavior of ceramic body (3).

Even with all these benefits, the whiskers are not widely used as a means of reinforcing because they are extremely expensive and difficult to produce; it is sometimes impractical to incorporate them within an array. The *in situ* growth of whiskers in a matrix is a promising way to overcome these drawbacks (4).

The present work aims to prepare mullite whiskers from powders of pure topaz doped with rare earths (REs). Mullite is an aluminosilicate which has been extensively investigated in recent decades because of their excellent mechanical properties, thermal shock resistance, creep resistance, low thermal conductivity and stability at high temperatures (5). It is the only compound thermodynamically stable in binary Al_2O_3-SiO_2, in the range 70.5 to 74.0wt% of Al_2O_3. In this range, according to the concentration of alumina varies in its chemical formula $3Al_2O_3.2SiO_2$ to $2Al_2O_3.SiO_2$ being called mullite 3:2 or 2:1 respectively. As a mineral, mullite is rare in nature and deposits existing reserves are small, preventing economic exploitation besides being protected by international convention (6).

Due to their low occurring in nature, mullites used in industry and research laboratories are synthesized and often costly. In general, synthesized mullite is 3:2 silica-rich (7).

An alternative process and less costly to produce mullite whisker high purity is by calcining colorless topaz. The colorless topaz is an abundant mineral in nature, and gemological worthless without economic application which facilitates their exploitation. The mullite produced has the ratio Al_2O_3:SiO_2 close to 2:1 that is rich in alumina (8).

The incorporation of ERs cations - La and Y - the structure of mullite from the topaz is made to investigate the effect of these dopants on the aspect ratio of the whiskers formed.

MATERIALS AND METHODS

Pellets of topaz powder and mixed with La_2O_3 and Y_2O_3 were uniaxially to 41Mpa for 5min. The pellets were heated at 1300°C and 1400°C-1h in static air in an oven tubular manufactured by Quimis, with a heating rate of 10°C/min. Table I shows

the identification of each sample with the concentrations by weight of La_2O_3 and Y_2O_3, and the treatments to which they were subjected.

Table I - Identification of topaz samples doped with La_2O_3 and Y_2O_3.

Samples	**La_2O_3 (%weigth)**	**Heating temperature**	**samples**	**Y_2O_3 (%weight)**	**Heating temperature**
TL3-1300	3	1300°C-1h	TY3-1300	3	1300°C-1h
TL3-1400	3	1400°C-1h	TY3-1400	3	1400°C-1h
TL5-1300	5	1300°C-1h	TY5-1300	5	1300°C-1h
TL5-1400	5	1400°C-1h	TY5-1400	5	1400°C-1h

Powders of La_2O_3 and Y_2O_3 with 99.99% purity were supplied by Vetec Fine Chemicals Ltd. and by Sigma-Aldrich in Brazil Ltda respectively. Samples Topaz northeastern Minas Gerais were selected based on their macroscopic aspects. The samples after fragmentation underwent an autogenous grinding the wet mill for 73h in jar with alumina ceramic coating manufactured by NTK technical ceramics. The granulometric analysis of the powder of topaz was performed on the analyzer laser particle size from CILAS, Model 1064. A solution of sodium hexametaphosphate 0.1%w/v was used as the dispersing agent. The diameter (D_{50}) was 3.42µm. Chemical analysis of topaz was performed by laboratory Lakefield Geosol Ltd. of Belo Horizonte, topaz showed a purity of 99.93% and a concentration of 54.9 wt% Al_2O_3, 32.55% SiO_2.

The crystallographic phases of topaz, of rare earth oxides, and mullites obtained were identified on a Shimadzu XRD-6000 diffractometer equipped with a cobalt tube and using iron filter. Scans were made between 7º and 70º with a speed of 2°/min and using silicon as internal standard. The lattice parameters were calculated using the program JADE after subtraction of the background and the contribution $K_{\alpha 2}$.

The thermal analysis (TGA-DTA) was performed on a device model SDT 2960 from TA Instruments. The temperature ranged from ambient to 1300°C with a heating rate of 10°C/min, using a constant flow of synthetic air and alumina crucible.

The microstructure of the samples of mullite was observed in a scanning electron microscope Jeol JSM 5510 the Laboratory of Microanalysis of DEGEO / UFOP.

RESULTS AND DISCUSSION

The X-ray diffractograms of Figure 1 show the effect of heating the topaz from colorless 1300° C and 1400° C for one hour in those temperatures. The only observed phase at the end of stage heating is mullite without glassy phase. The presence of peak silicon is due to its use as an internal standard for calculating network parameters.

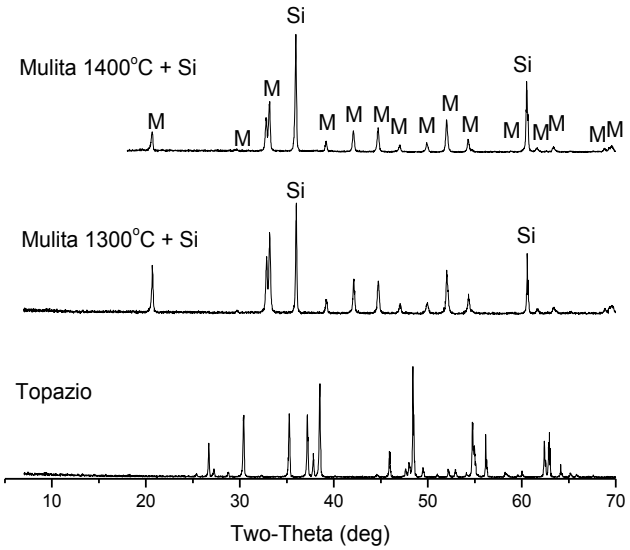

Figure 1: X-ray diffractograms of samples colorless topaz and treated at 1300°C and 1400°C.

The micrograph of mullite formed revealed microstructure whiskers with high porosity. The gases released during decomposition of topaz are responsible for open porosity observed. The microstructure of mullite obtained Topaz, consisting of whiskers containing porosity, represents an intrinsic characteristic associated with the decomposition of that mineral.

Thermal Analysis and X-ray Diffraction

Figure 2 shows the differential thermal analysis (DTA) made from powders of topaz, La_2O_3 and Y_2O_3 and comparison with the powders doped.

Topaz is an aluminosilicate chemical formula $Al_2SiO_4(OH_{1-x}F_x)_2$. Its DTA curve shows two endothermic peaks, an 1186.49°C and another at 1235.93°C. These peaks correspond to the loss of hydroxyl and gas releases in the form of SiF4, HF and AlOF respectively. Fluoride to leave the structure of topaz drags silicon having initiated the transformation of mullite. The temperature of mulitization can be considered to be 1236°C. The mass loss on decomposition of topaz was approximately 20%.

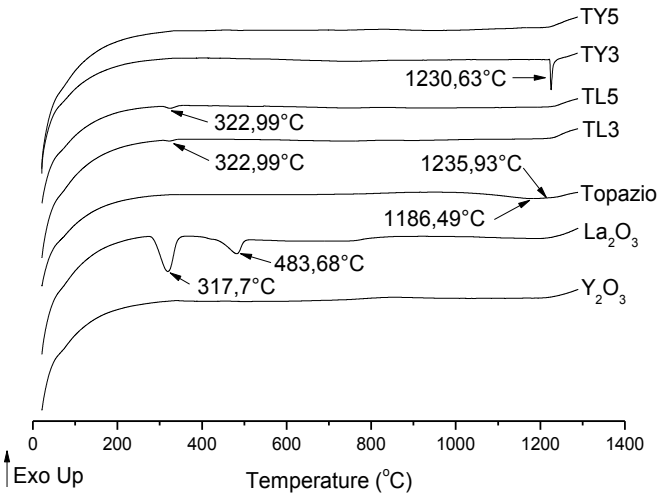

Figure 2: Differential thermal analysis (DTA) of pure and doped powders.

The DTA curve for Y_2O_3 is stable throughout the temperature range worked. The same is not true for the stability La_2O_3. The rare earth oxides are hygroscopic and can absorb water and CO_2 from the atmosphere, the presence of hydroxides and carbonates in the powder of La_2O_3 is normal (9). X-ray analysis revealed the presence of La $(OH)_3$ and $La_2O_2CO_2$. The first endothermic peak at 317.7°C corresponds to the second peak dehydration, loss of carbonate.

The DTA curves for sample TL3 and TL5, exhibit an endothermic peak in the temperature of 322.99°C related to dehydration and release of CO_2 samples, because nothing happens to the topaz in this temperature range. The mass loss was around 24.0%. For samples TY3 and TY5 curves are very stable and showed a mass loss of about 23.0%.

Figure 3 shows the differential thermo gravimetric (DTG) of the samples. Note that the addition of La_2O_3 or Y_2O_3 lowers the mulitization temperature of the topaz. This favors the formation of inducing the growth of mullite whiskers

Figure 4 shows the x-ray diffractograms of the samples doped with La_2O_3. The lanthanum oxide is all consumed during the reactions, not forming complex phases. Mullite and alumina are the only phases present. The peaks related to alumina are marked with (+), the other unmarked peaks correspond to mullite.

Figure 5 shows X-ray diffractograms of the samples as Y_2O_3 doped. Not every Y_2O_3 is consumed during the reactions of transformation of mullite. Besides alumina and mullite phases as a result, there is the presence of crystalline phases $Y_2Si_2O_7$ (yttrium disilicate) and the oxide non-stoichiometric $YO_{1.335}$. When we increased the

concentration of Y_2O_3, TY5 samples, phase $YO_{1,335}$ disappears at 1400°C. The DTA analysis, although made up to 1300°C, does not show any peak of the formation of these crystalline phases, they may be occurring together with the formation of mullite.

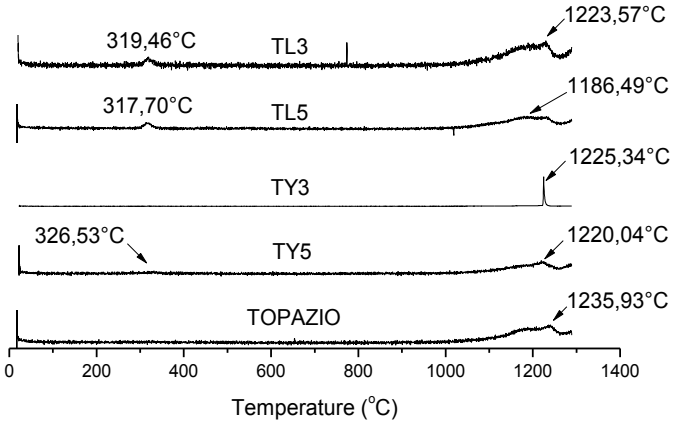

Figure 3: Differential Thermo Gravimetric (DTG) topaz and doped samples.

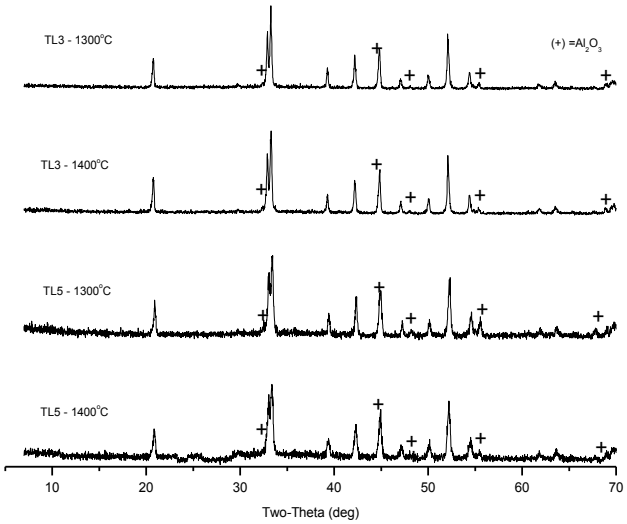

Figure 4: X-ray diffractograms of the samples doped with La_2O_3.

The yttrium disilicate - $Y_2(Si_2O_7)$ - is a sorosilicate (Si_2O_7) that has six polymorphic phases at high temperatures, (y, α, β, γ, δ and probably z). The phase changes occur at temperatures 1050°C for polymorphic phase y, 1225°C to α, 1445°C to β and 1535°C to γ, with change of density 4.30, 4.03, 4.04 and 4.11g/cm^3 phases α, β, γ, δ respectively. It is a highly refractory silicate with a melting point of 1775°C, which makes a ceramic with potential for high temperature applications. Obtaining $Y_2Si_2O_7$

through synthesis is expensive and requires a relatively long time (10). The presence of this phase in mullite can also improve their thermo mechanical properties.

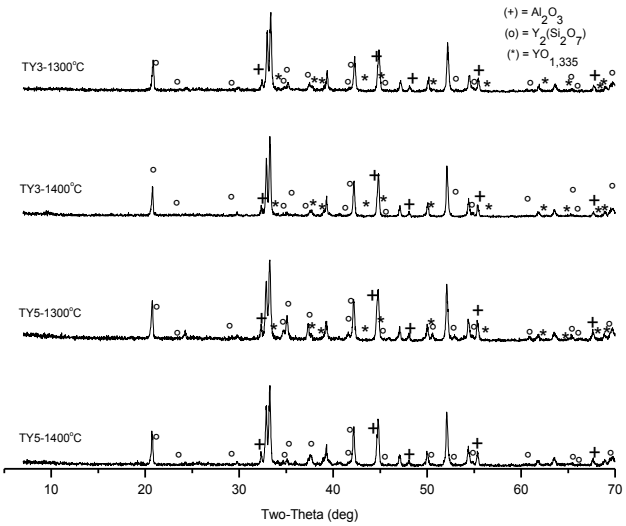

Figure 5: X-ray diffractograms of the samples doped with Y_2O_3. Representation: (+) Al_2O_3 (o) $Y_2Si_2O_7$, (*) $YO_{1,335}$, unmarked peaks correspond to mullite.

Scanning Electron Microscopy - SEM

Figure 6 shows a SEM micrograph of the sample TL3-1400°C, one observes the presence of some whiskers well developed. This is because of their training in a glassy phase.

Figure 7 shows the SEM micrograph of the sample TY3-1300°C where it appears somewhere radial growth of whiskers. The whiskers are shown covered by a glassy phase, motive of appearance blurry middle. The whiskers formed are shorter and thicker compared with that of Figure 6.

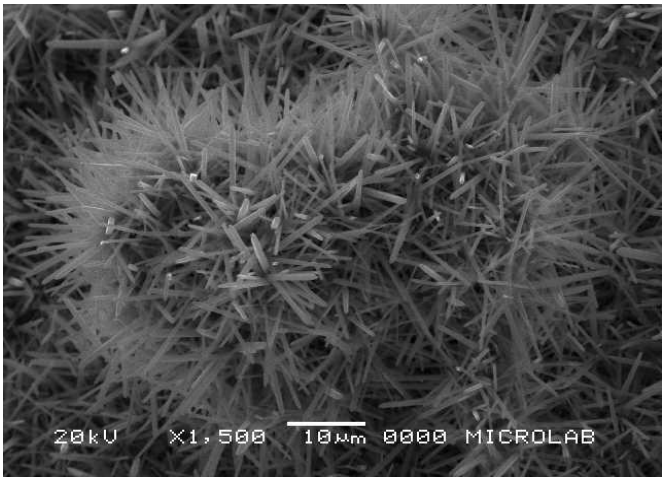

Figure 6: SEM micrograph of the sample TL3 1400°C - 1h

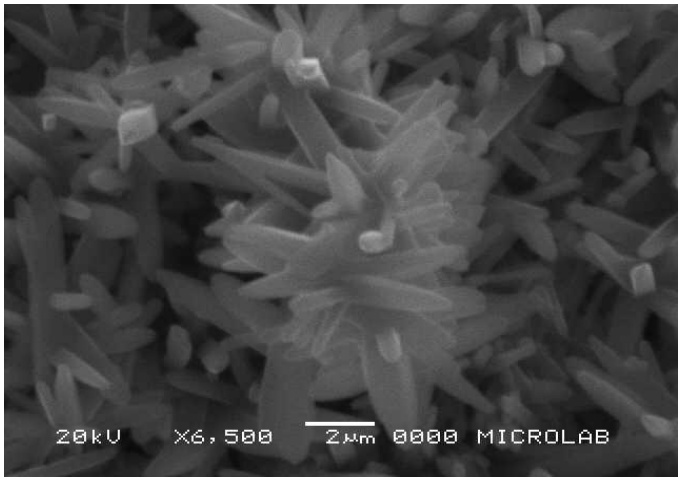

Figure 7: SEM micrograph of the sample TY3 1300°C - 1h

Characterizations of chemical and crystallographic mullites and whiskers

The composition of mullite can be estimated empirically from the constant "a" of the lattice. Knowing the value of the parameter "a" in Angstrom (Å), one can calculate the molar percentage "m" of Al_2O_3 in mullite by the following equation (A) (11).

$$m = 144,5.a – 1029,5 \qquad (A)$$

The chemical formula for mullite is described as being $Al_{4+2x}Si_{2-2x}O_{10-x}$, where "x" represents the number of vacancy oxygen per unit cell (12). The x value can be determined on the basis of Al_2O_3 molar concentration (m), according to equation (B) (11).

$$x = 10 – 6[(m+200)/(m+100)] \qquad (B)$$

Table II shows the parameters of the network formed mullites, calculated using the software JADE, Al_2O_3 molar concentrations according to equation (A), the values of "x" according to equation (B), and the ratio Al_2O_3: SiO_2.

The mullite formed by calcination Topaz has the ratio Al_2O_3:SiO_2 close to 2:1 which is rich in aluminum and has a low solubility of foreign cations in its structure. However, a mullite-rich alumina favors the growth of acicular grains (13). Any process mullite formation that allows the control to its chemical composition, indirectly controls the microstructure and the mechanical properties of mullite formed. In general, the addition of any oxide in the synthesis of mullite, besides increasing the glassy phase

formation, reduces its viscosity, which favors the formation of mullite, the anisotropic growth and dimensions of the whiskers (14). The alumina is sensitive to the presence of a glassy phase, it precipitates in this phase and dissolves forming mullite. The lower the viscosity of the glassy phase, the better the process of precipitation and dissolution of alumina. Any factor that contributes to enhance the formation of a vitreous phase and low viscosity is useful to reduce the mulitization temperature.

Table II - Characterization of mullites formed

Samples	**Network parameters (Å)**			**% moles Al_2O_3**	**x**	**Al_2O_3:SiO_2**
	a	b	c			
MUL-1300	7.573043	7.679319	2.890517	64.80	0.359	2.36:1.28
TL3-1300	7.557852	7.678665	2.885647	62.61	0.310	2.31:1.38
TL5-1300	7.563316	7.680342	2.886761	63.40	0.328	2.33:1.34
TY3-1300	7.556729	7.679457	2.885241	62.45	0.306	2.31:1.39
TY5-1300	7.554075	7.678133	2.887413	62.06	0.298	2.30:1.40
MUL-1400	7.561808	7.688444	2.887244	63.18	0.323	2.32:1.35
TL3-1400	7.557053	7.681457	2.886546	62.49	0.307	2.31:1.39
TL5-1400	7.562429	7.679133	2.885683	63.27	0.325	2.32:1.35
TY3-1400	7.556655	7.680898	2.885634	62.44	0.306	2.31:1.39
TY5-1400	7.558572	7.681414	2.887092	62.71	0.312	2.31:1.38

The addition of ERs oxides reduces the concentration of alumina to silica increases. It also reduces the value of x, decreasing the amount of oxygen vacancy in the structure. The addition of 3% La_2O_3 or Y_2O_3 reduces the lattice parameters of mullite, however, for the addition of 5%, the parameters tend to increase when incorporating La_2O_3, but adding Y_2O_3 tends to further reduce the parameters "a" and "b" and increases the parameter "c".

Table III shows the dimensions and the aspect ratio of whiskers mullites formed by calcining powders of pure and doped topaz. The ERs oxides strongly decrease the aspect ratios of the whiskers formed in relation to pure mullite. This reduction is more marked for mullite doped Y_2O_3, being 77.5% at 1300°C for 5% of the oxide, and 79.3% at 1400°C, for 3% of dopant. While the addition of La_2O_3 reduces the size of whisker, Y_2O_3 reduces the length but increases the thickness of the whiskers.

In the system Ln_2O-Al_2O_3-SiO_2 glass area decreases with cationic field strength (CFS) given by z/r^2, where z is the valence of the cation and r is ionic radius. For La^{3+} is 2.268Å^{-2}, and for Y^{3+} is 3.469Å^{-2}. The glass transition temperature (*tg*) increases linearly with the CFS, as the molar volume decreases. The region of ternary glass formation of aluminosilicate containing REs elements becomes smaller when the ionic radius REs element decreases (15).

Table III - Dimensions and aspect ratio (AR) of whiskers formed.

Samples	**Dimension of whiskers (μm)**		**R.A**	**Samples**	**Dimension of whiskers (μm)**		**R.A**
1300	**length**	**width**		**1400**	**length**	**width**	
MUL	12.92±218	0.46±0.08	28.09	MUL	11.64±1.39	0.37±0.08	31.46
TL3	6.76 ±0.91	0.42±0.19	16.09	TL3	7.77 ±1.27	0.55±0.10	14.13
TL5	5.29 ±0.74	0.36±0.14	14.69	TL5	6.22 ±1.53	0.42±0.14	14.81
TY3	4.34 ±1.08	0.59±0.15	7.35	TY3	4.13 ±1.24	0.64±0.12	6.45
TY5	3.73 ±0.74	0.59±0.15	6.32	TY5	4.37 ±1.46	0.64±0.17	6.87

The ionic radius of $Y^{3+}$is 0.93Å and La^{3+} is 1.15 Å, the CFS Y^{3+} is higher than that of La^{3+}. The glassy phase formed by Y_2O_3 in the decomposition of topaz would be smaller than that formed by La_2O_3. Accordingly, for the samples doped with Y_2O_3, there would be a glassy phase sufficient for the complete development of whiskers, they would be smaller in length and thicker. Another factor that contributes to low formation of the glass phase is that part of Y_2O_3 react with the silica and oxygen not to form a glassy phase but to form a crystalline phase $Y_2Si_2O_7$ and $YO_{1.335}$.

CONCLUSIONS

Is possible to change the aspect ratio and size of mullite whiskers from the calcination of topaz doping it with La_2O_3 or Y_2O_3. The addition of these oxides reduces the aspect ratio, particularly when dopa with Y_2O_3. Unlike La_2O_3, Y_2O_3 favors the formation of other crystalline phases, since the CFS for Y^{3+} is greater than for La^{3+}. The crystalline phases formed are $Y_2Si_2O_7$, which can improve the thermo mechanical properties of mullite, non-stoichiometric oxide $YO_{1.335}$ and the appearance of a glassy phase. The addition of ERs oxides increases the concentration of silica, decreases

alumina the concentration and mulitization temperature. The reactions that occur due to transport of gases - SiF_4, HF, and AlOF - are responsible for the formation of whiskers during decomposition of pure topaz. Another secondary process - precipitation and dissolution of alumina - also acts in the formation of whiskers due to the addition of ERs oxides. The whisker from the decomposition of topaz has a low manufacturing cost and ratio Al_2O_3:SiO_2 is close to 2:1, rich in alumina.

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