ALTERATION OF PEROVSKITE TO ANATASE IN SILICA-UNDERSATURATED ROCKS OF THE CATALÃO-I CARBONATITE COMPLEX, BRAZIL: A RAMAN STUDY

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Resumo *ALTERATION OF PEROVSKITE TO ANATASE IN SILICA-UNDERSATURATED ROCKS OF THE CATALÃO-I CARBONATITE COMPLEX, BRAZIL: A RAMAN STUDY* A transformação de perovskita para anatásio decorrente da intrusão de um carbonatito foi investigada usando microsonda eletrônica, imagens de elétrons retroespalhados, mapas de distribuição de elementos por dispersão de energia e perfis de composições químicas no microscópio eletrônico de varredura e espectroscopia Raman. Os cálculos de balanço de massa entre a perovskita e o anatásio permitiram verificar que com o processo de alteração houve a lixiviação de Ca, Nd, Ce e Na e a concentração relativa de Ti, Si, Mg, Zr, Nb e Fe. A presença de uma “camada de Ti” amorfa (> 1 mm) na superfície dos grãos foi investigada. Os espectros Raman confirmam a existência de uma fase intermediária composta por perovskita alterada anterior a cristalização do anatásio. Não foi possível reconhecer um limite entre a perovskita alterada e a inalterada devido a heterogeneidade no processo. A estrutura da perovskita muda antes da lixiviação do cálcio. O processo culmina com a cristalização de anatásio, quando o cálcio é lixiviado e a estrutura colapsa. O processo de alteração pela ação do fluido carbonatítico é diferente daquele descrito na literatura, onde o cálcio é lixiviado em dois estágios para formar o anatásio.

Palavras-chave: perovskita, anatásio, Catalão-I, espectroscopia Raman, Brasil.

Abstract The transformation of perovskite into anatase due to a carbonatitic emplacement was investigated using electron microprobe, back-scattered electron images, element-distribution maps, chemical composition profiles and Raman spectroscopy. The mass balance calculations between perovskite and anatase indicate that Ca, Nd, Ce and Na are leached and Ti, Si, Mg, Zr, Nb and Fe are relatively concentrated. The presence of an amorphous “Ti-layer” (> 1 mm) on the surface of the grains was investigated. Raman spectra confirm the existence of an intermediate phase composed by altered perovskite previously to the anatase crystallization. It is not possible to recognize a limit between the unaltered and altered perovskite, due to the heterogeneity of the process. The perovskite structure changes before the leaching of calcium. This process culminated with the crystallization of anatase when the calcium is leached and the structure collapses. The alteration process by the carbonatic fluid action is different from that induced by weathering which promote the leaching of calcium and the anatase genesis in two stages.

Keywords: perovskite, anatase, Catalão-I, Raman spectroscopy, Brazil.

INTRODUCTION Perovskite, ideally CaTiO_3 , is a ubiquitous accessory mineral in SiO_2 -undersaturated rocks such as kimberlites, melilitites, foidites, olivinites, clinopyroxenites and carbonatites. It is also the principal component of a synthetic assemblage of titanate phases known as SYNROC, a potential nuclear waste form (Ringwood *et al.* 1979). Depending on $\text{P}(\text{CO}_2)$, perovskite is a stable phase in many magmatic assemblages. However, thermodynamic calculations have clearly shown that perovskite is unstable at low temperatures. Alteration of perovskite by subsolidus re-equilibration, metasomatic and secondary alteration, produces other Ti-bearing minerals such as titanite and TiO_2 polymorphs [rutile, anatase and brookite, $\text{TiO}_2(\text{B})$] ilmenite, and $(\text{Nb}, \text{Ti}, \text{Fe}, \text{Ta})_2\text{O}_5$ (Mitchell & Chakhmouradian 1998, Chakhmouradian & Mitchell 2000). The alteration processes which transforms perovskite to metastable TiO_2 polymorphs anatase, brookite and $\text{TiO}_2(\text{B})$ instead of rutile is poorly understood (Banfield, *et al.*, 1991a and b). The difference between the stabilities of these minerals is small at low temperatures (Post & Burnham 1986). However, anatase is the most stable polymorph in alkaline rocks and

associated carbonatites from Alto Paranaíba alkaline province (Brazil). The presence of rare-earth oxides seems to facilitate crystallization of anatase (Hishita *et al.* 1983). The mechanism that controls such alteration has been the subject of many studies.

The alteration of perovskite to anatase from the Catalão-I Alkaline Complex (Brazil) was studied using Raman spectroscopy, element-distribution maps, chemical profiles and electron microprobe analysis. The primary objective of our study was discuss the process of alteration of perovskite to anatase. According to Banfield & Veblen (1992), Jostons *et al.* (1990) summarized an experimental work on perovskite dissolution including data of Pham *et al.* (unpublished data) which suggest that under epithermal conditions an amorphous film forms on the perovskite surface. Another objective is to investigate the presence or not of an amorphous Ti-rich layer larger than 1 μm .

Banfield & Veblen (1992), in transmission-electron microscopy studies, did not present any evidence for an amorphous Ti phase along the interface between anatase and perovskite. In this case, the alteration should occur by incongruent dissolution of

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secondary paragenesis. Then, in Catalão I, the ilmenite and anatase genesis does not follow the reaction described above. In this alkaline massif, with the alteration process, REE and other elements concentrated in the perovskite are leached and precipitated as Ba-LREEC carbonate (see Fig. 1). The absence of titanite reflects the overall low activity of silica in the carbonatite system.

The analyses of perovskite are presented in Table 1 and of anatase in Table 2. The perovskite and anatase totals are around 97% probably due the presence of REE not analyzed, the microporosity, and the presence of crystalline defects.

Ca, Ti, Si, Mg, Nb, Zr, Na, Fe and Ce distribution maps were made on the same region where compositional profiles, EDS, EMPA and Raman analyses were done (see Fig. 1). The analyzed area is chosen after optical microscopic observations where perovskite is partially replaced by anatase. The element distribution maps indicated that Ca, Ti, Si and Mg have different concentrations in the sample. Elevated Si and Mg define the areas of altered olivine; while Ca marks the perovskite and Ti, the anatase (Fig. 2). The map of Ca distribution shows high Ca contents in the perovskite and much lower in anatase. This element was leached during the pseudomorphic alteration. Chemical analyses do not show any variation in the level of Ca across the perovskite grain. It is interpreted here as a consequence of “total” leaching of Ca from perovskite grain with no intermediate Ca phases.

Mass balance calculations, using the equations proposed by Gresens, 1967, were made for the pair perovskite-anatase (using Ti as immobile element). It indicate that Ca, Nd, Ce and Na are leached and Ti, Si, Mg, Zr, Nb and Fe are relatively concentrated. According to Myhra *et al.* (1984), perovskite-type rapidly equilibrates with the fluid phase through precipitation of alkaline-earth carbonates and development of a surface layer enriched in TiO_2 . The map of Ti

distribution and the chemical analyses along the PA profile (Fig. 1) show that similar processes occurred at Catalão I. Ti behaves as “immobile” element during the alteration process.

RAMAN SPECTROSCOPY The perovskite and anatase were also examined using Raman spectroscopy. Raman spectra were acquired along the PA profile (Fig. 1). According to Gillet *et al.* (1993), Raman spectra of perovskite typically consist of two broad bands at 150-600 and 650-850 cm^{-1} . On the lower frequency band (150-600 cm^{-1}), sharp peaks are superimposed. The spectra of Catalão-I perovskite (Fig. 3) are similar to those described by Gillet *et al.* (1993), but three additional broad bands appear in the lower frequencies region (509, 635, 794 cm^{-1}). The analysis P4 (Fig. 3a) presents a peak at 400 cm^{-1} that in other perovskite analyses (P1, P2, P3 and P5) appears as a band. The vibration at 470 cm^{-1}

Figure 2 - Maps of Ca, Ti, Si and Mg distributions.

Figure 3 - Raman spectra of perovskite, altered perovskite and anatase.

Table 1 - Chemical composition of perovskite from Catalão I Alkaline Complex.

Sample	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10
CaO	34.90	35.05	34.68	34.85	35.13	35.11	34.89	34.84	34.90	34.81
Na ₂ O	0.65	0.58	0.60	0.65	0.59	0.56	0.57	0.48	0.58	0.60
La ₂ O ₃	1.32	1.26	1.28	1.33	1.29	1.30	1.32	1.26	1.39	1.39
Ce ₂ O ₃	3.20	3.15	3.09	3.73	3.14	3.17	3.31	3.05	3.07	3.08
Nd ₂ O ₃	0.90	1.17	1.15	1.07	0.99	1.01	1.06	1.05	1.05	1.06
MgO	0.02	0.02	n.d.	0.01	n.d.	n.d.	0.02	0.01	0.01	n.d.
Fe ₂ O ₃	1.82	1.79	1.77	1.67	1.73	1.68	1.70	1.69	1.81	1.74
TiO ₂	53.91	53.15	54.10	53.41	53.34	53.31	53.37	52.99	52.73	53.42
Nb ₂ O ₃	0.93	0.93	0.78	0.76	0.77	0.82	0.87	0.92	0.81	0.89
ZrO ₂	0.12	0.17	0.13	0.17	0.19	0.19	0.25	0.22	0.31	0.17
SiO ₂	0.03	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.
Total	97.80	97.28	97.58	97.65	97.17	97.15	97.36	96.51	96.67	97.16
Structural formulae based on 3 atoms of oxygen										
Ca	0.90	0.91	0.89	0.90	0.91	0.91	0.90	0.91	0.91	0.90
Na	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02	0.03	0.03
La	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ce	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Nd	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Ti	0.97	0.97	0.98	0.97	0.97	0.97	0.97	0.97	0.96	0.97
Nb	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Total	1.99	2.00	1.99	2.00	1.99	2.00	1.99	1.99	1.99	1.99

* Strontium in all perovskite analyses was below detection limits.

** Iron as Fe³⁺, according to Muir *et al.* (1984).

n.d. = not detected

Table 2 - Chemical composition of anatase from Catalão I Alkaline Complex.

Sample	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10
SrO	n.d.	n.d.	0.01	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CaO	0.12	0.18	0.17	0.19	0.13	0.14	0.46	0.39	0.16	0.24
Na ₂ O	n.d.	0.02	n.d.	0.01	n.d.	n.d.	n.d.	0.04	n.d.	n.d.
La ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ce ₂ O ₃	0.23	0.20	0.21	0.36	0.04	0.14	0.17	0.23	0.15	0.07
Nd ₂ O ₃	0.04	n.d.	n.d.	0.09	0.07	n.d.	0.03	n.d.	n.d.	n.d.
MgO	0.04	0.05	0.04	0.09	0.02	0.03	0.03	0.03	0.01	0.01
Fe ₂ O ₃	2.21	2.11	1.40	1.87	1.93	1.78	2.68	2.85	2.69	2.07
TiO ₂	92.64	93.27	93.16	92.39	93.34	93.68	91.89	92.91	92.35	93.86
Nb ₂ O ₃	1.42	1.32	1.74	1.59	1.47	1.27	1.80	1.49	1.44	1.47
ZrO ₂	0.34	0.24	0.28	0.22	0.25	0.30	0.38	0.29	0.33	0.23
SiO ₂	0.37	0.47	0.44	0.69	0.24	0.15	0.31	0.22	0.33	0.22
Total	97.41	97.86	97.45	97.54	97.49	97.49	97.75	98.45	97.46	98.17
Structural formulae based on 2 atoms of oxygen										
Ca	0	0	0	0	0	0	0.01	0.01	0	0
Fe	0.02	0.02	0.01	0.02	0.02	0.02	0.03	0.03	0.03	0.02
Ti	0.97	0.97	0.97	0.96	0.97	0.97	0.96	0.96	0.96	0.97
Nb	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Si	0.01	0.01	0.01	0.01	0	0	0	0	0	0
Total	1.01	1.01	1.00	1.00	1.00	1.00	1.01	1.01	1.00	1.00

** Iron as Fe³⁺, according to Muir *et al.* (1984).

n.d. = not detected

Table 3 - Raman modes of perovskite and anatase from Catalão I Alkaline Complex.

Perovskite												Anatase				
P 1	P 2	P 3	P 4	P 5	P 6	PA 1	PA 2	PA 3	PA 4	PA 5	PA	A 1	A 2	A 3	A 4	A 5
364(?)	368(?)	366(?)		368	362			364	368	364	366					
395	387	392	408	407	389	405	406	410	400	395	396	395	395	395	398	398
470	470	470	469	471	471	469	470	465	470							
519	509	496	511	503	507			518	518	517	517	517	516	517	519	519
				534	531	524	530									
655	655	658	647	627	646	657		639	639	639	639	638	638	638	640	640
						675										
793	792	795	797	795	821	784	784									

correspond to a sharp peak in all unaltered perovskite analyses.

Table 3 presents the Raman modes of perovskite and anatase from Catalão-I (sites of analyses in Fig. 1).

With alteration, some perovskite bands become broader, change their frequency, decrease its intensity, or disappear (Table 1 and Fig. 3). The 387-395 cm^{-1} perovskite band decreases in amplitude and shifts to 405-406 cm^{-1} . The 395 cm^{-1} band reappear in anatase as a sharp peak. The 496-519 cm^{-1} band has a large vibration mode. In the altered perovskite, it is located at 517-519 cm^{-1} , that is preserved in the anatase structure. The position of the 627-585 cm^{-1} band shifts with alteration to 639 cm^{-1} , and does not change in the anatase spectra. The vibration modes that are destroyed by the alteration and do not appear in the anatase spectra are described below. The 364-368 cm^{-1} band has larger variations in amplitude and in some spectra it does not appear. A characteristic 465-470 cm^{-1} sharp peak persists in the perovskite spectra to the final stage of alteration, but disappears in the anatase spectra. The 524-534 cm^{-1} band is a vibration mode that occurs in some perovskite analyses. The 675 cm^{-1} band appears only in the spectrum of the altered perovskite. However, the 784-821 cm^{-1} band disappears at the “beginning” of the alteration. These variations in the frequency and amplitude of the Raman modes probably reflect the chemical heterogeneity of our samples (see Fig. 2). With the leaching of calcium the structure collapses to form anatase.

It is possible to verify that the amplitude of some spectral bands increases from the unaltered to the altered perovskite, as the 518 and 639 bands in the PA3 sample. This increase probably indicates changes in the orientation of TiO_6 that modify the vibration modes. A similar process occurs in connection with the upon transition of the altered perovskite to anatase.

DISCUSSIONS AND CONCLUSIONS Field observations and laboratory analyses of Catalão I rocks made possible the identification of “phoscorites” and pyroxenites followed by the intrusion of carbonatites. The reaction with CO_2 generated a secondary paragenesis composed of tetraferriphlogopite, anatase and Ba-LREE carbonate. The rare-earth elements are inherited from the perovskite and Ba is probably derived from the carbonatitic fluid. The leaching of calcium from the perovskite and magnesium from the olivine contributed to the crystallization of dolomite.

The Raman spectra between perovskite and anatase confirm that there is an alteration front. However, it does not show a “pure amorphous Ti-layer” (> 1 mm) at the transitional region. All analyses show the TiO_6 vibration modes and the increase of background intensity that could be related with the presence of an amorphous phase or the presence of weakly bonded water molecules or structural groups, as described by Nasdala *et al.* (1995) to

metamictized zircons.

The Raman spectra confirm the existence of an intermediate phase composed by altered perovskite preceding the crystallization of anatase. This phase is characterized by some perovskite peaks that did not change their frequency and amplitude during alteration. Some bands are destroyed before the structural change that forms anatase. Their relative intensity probably decreases with the increase of alteration. The vibration modes which persist through the alteration indicate that there is not a total dissolution of crystals. The alteration of perovskite by the carbothermal fluid culminates with the crystallization of anatase when the calcium is “completely” leached and the structure collapses. It does not follow the stepwise conversion proposed by Banfield & Veblen (1992) that involves calcium leaching in two stages during weathering of perovskite to anatase. In both processes the structural mechanisms responsible for the perovskite (corner-sharing octahedra) alteration to anatase (edge-sharing octahedra) are continuing to be unclear. The fundamental building-blocks approach (Moore 1986, Veblen 1991) continues not being understood in this case. The limit between altered and unaltered perovskite is unclear because it is an heterogeneous alteration and different Raman vibration modes behave differently. The bands in altered perovskite shift, become broader and change intensity probably due to the increase of disorder of the octahedra orientations, and due to the presence of submicron domains of anatase and/or an amorphous phase. So, the Raman spectra of altered perovskite contain bands that correspond to the sharp peaks of anatase.

Raman spectroscopy does not permit to verify if the reaction involves direct structural inheritance, but it provides evidence that an intermediate phase occurs before the collapse of perovskite structure to form anatase.

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