

## Electronic Supplementary Information

### Incorporation of Vanadium in the Framework of Hydroxyapatites: Importance of the Vanadium Content and pH Conditions during the Precipitation Step.

Sarah Petit,<sup>a,b</sup> Thrimurthulu Gode,<sup>a</sup> Cyril Thomas,<sup>a</sup> Stanislaw Dzwigaj,<sup>a</sup> Yannick Millot,<sup>a</sup>

Dalil Brouri,<sup>a</sup> Jean Marc Krafft,<sup>a</sup> Gwenaëlle Rousse,<sup>c</sup> Christel Laberty-Robert,<sup>b</sup> Guylène

Costentin<sup>a\*</sup>

<sup>a</sup> Sorbonne Universités, UPMC Univ Paris 06, CNRS, UMR 7197, Laboratoire Réactivité de Surface, F-75005 Paris France.

<sup>b</sup> Sorbonne Universités, UPMC Univ Paris 06, CNRS, Collège de France, Laboratoire Chimie de la Matière Condensée de Paris, 11 place Marcelin Berthelot, 75231 Paris, France

<sup>c</sup> Sorbonne Universités, UPMC Univ Paris 06, Collège de France, Chimie du Solide et de l'Energie, Collège de France, 11 Place Marcelin Berthelot, 75231 Paris, France

#### **S1: Chemical composition obtained by ICP analysis.**

**Table S1** reports the results from ICP analysis. The theoretical composition reported correspond to the target prepared compound  $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{VO}_4)_x(\text{OH})_2$  (started from stoichiometric precursors) The chemical compositions deduced from ICP analysis for the  $\text{V}_x$ -HAp-pH-9 series are in good agreement with the theoretical ones, leading to stoichiometric compounds ( $\text{Ca}/(\text{P}+\text{V}) \sim 1.67$ , except for  $x$  value = 6. For the  $\text{V}_x$ -HAp-pH-per series, it appears that most of the  $\text{Ca}/(\text{P}+\text{V})$  ratios are substantially different from 1.67, which is characteristic of

either under-stoichiometric or over-stoichiometric samples and was further explained by the concomitant formation of  $\text{Ca}_2\text{V}_2\text{O}_7$  phase from  $x \geq 4$  values, and even for the formation of this lone phase for  $x = 6$ .

In addition, the good concordances obtained for the chemical compositions measured for  $\text{V}_6$ -HAp-pH-per and for  $\text{Ca}_2\text{V}_2\text{O}_7$  sample are consistent with the identification of pure  $\text{Ca}_2\text{V}_2\text{O}_7$  phase formed in  $\text{V}_6$ -HAp-pH-per sample.

**Table S1.** Chemical composition for the two series of samples

	x value	Composition ( $\text{mol g}^{-1} \times 10^{-5}$ )									
		Ca		P		V		P+V		Ca/(P+V)	
		th	exp	th	exp	Th	exp	th	exp	th	exp
$\text{V}_x$ - HAp- pH-9	0.00	9.95	9.68	5.98	5.86	0	0	5.98	5.86	1.67	1.65
	0.28	9.90	9.76	5.66	5.49	0.27	0.25	5.93	5.73	1.67	1.70
	0.55	9.85	9.78	5.37	5.30	0.55	0.45	5.952	5.75	1.67	1.70
	0.78	9.75	9.57	5.15	4.11	0.76	0.64	5.92	5.75	1.67	1.67
	1.38	9.70	9.54	4.48	4.50	1.3	1.20	5.81	5.70	1.67	1.67
	2.00	9.58	9.45	3.83	3.86	1.92	1.82	5.75	5.68	1.67	1.66
	3.00	9.40	9.27	2.82	2.87	2.82	2.71	5.64	5.58	1.67	1.66
	4.00	9.23	9.09	1.85	1.88	3.69	3.65	5.53	5.53	1.67	1.67
	5.22	8.95	8.87	0.25	7.39	5.12	4.61	5.37	5.35	1.67	1.66
	6.00	8.90	8.76	0	0	5.33	4.96	5.33	4.96	1.67	1.76
$\text{V}_x$ - HAp- pH-per	0.00	9.95	9.75	5.98	5.89	0	0	5.98	5.89	1.67	1.65
	0.28	-	-	-	-	-	-	-	-	-	-
	0.55	9.85	9.90	5.37	5.31	0.55	0.49	5.92	5.31	1.67	1.71
	0.78	9.75	9.53	5.15	5.35	0.76	0.76	5.92	6.11	1.67	1.56
	1.38	9.70	9.68	4.48	4.60	1.33	1.29	5.81	5.90	1.67	1.64
	2.00	9.58	9.61	3.83	4.04	1.92	1.93	5.75	5.97	1.67	1.61
	3.00	-	-	-	-	-	-	-	-	-	-
	4.00	-	-	-	-	-	-	-	-	-	-
	5.22	8.95	8.87	0.25	0.94	5.12	5.20	5.37	6.14	1.67	1.44
	6.00	8.90	6.81	0	0	5.33	6.71	5.33	6.71	1.67	1.02
$\text{Ca}_2\text{V}_2\text{O}_7$	-	6.66	6.80	0	0	6.80	6.57	6.80	6.57	1.00	1.04

## S2 : $\text{Ca}_2\text{V}_2\text{O}_7$ synthesis :

The synthesis of the pure  $\text{Ca}_2\text{V}_2\text{O}_7$  phase was adapted from Gao and al. who described a preparation of  $\text{Mg}_2\text{V}_2\text{O}_7$  <sup>1</sup>.by the citrate method with the nominal Ca/V atomic ratio equal to 1/1. First, 250 mL of an aqueous solution of 0.1 mol. L<sup>-1</sup> of  $\text{NH}_4\text{VO}_3$  (beforehand heated to 333 K to dissolve the solid) was mixed to the equivalent of 0.1 mol. L<sup>-1</sup> of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and heated under reflux at 363 K during two hours. The resulting color of the solution is light yellow (**Fig S2.1a**). After cooling down to RT, 2 mL

of nitric acid 68% were added to prevent the precipitation. The solution turned to orange, reaching a pH value of 3 and was left under magnetic stirring overnight (**Fig S2-1.b**). Citric acid was added in order to counterbalance all the positive charges of cations ( $2 \text{ Ca}^{2+}$  and  $2 \text{ V}^{5+}$  in  $\text{Ca}_2\text{V}_2\text{O}_7$ ). Given the 3 negative charges per molecules of citric acid, 22.430 g (0.467 moles) of citric acid was incorporated within 10 minutes and the solution was left under stirring at RT for 3h. It turned to olive green (**Fig S2-1.c**). A progressive and slow evaporation of the solution under vacuum by using a Rotavapor was started at 333K. The solution turned emerald green and then royal blue (**Fig S2-1.d**). By increasing the temperature to 353 K, the solution became viscous and at 363 K a green foam was formed which turned brown as it was totally dried (**Fig S2-1.e**) The obtained solid was crushed and calcined at 653K for 18h and then at 823K for 6h. A final light yellow powder was obtained (**Fig S2-1.f**).

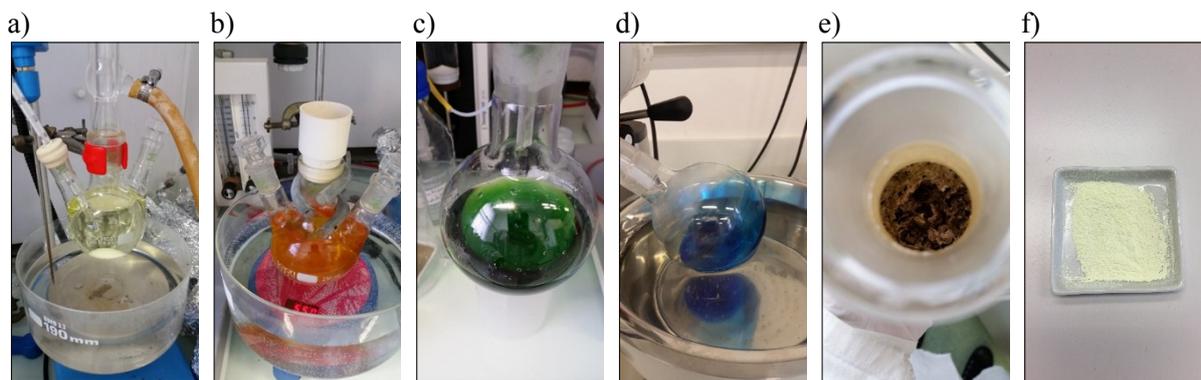


Figure S2-1: Change of color during the different steps of the synthesis of the solid  $\text{Ca}_2\text{V}_2\text{O}_7$ .

The XRD pattern of the powder reported in **figure S2-2** could be indexed using the JCPDS 038–0284 file, which is indicative of the formation of crystalline  $\text{Ca}_2\text{V}_2\text{O}_7$  phase. This result is fully consistent with the chemical analysis data reported above in **Table S1**.

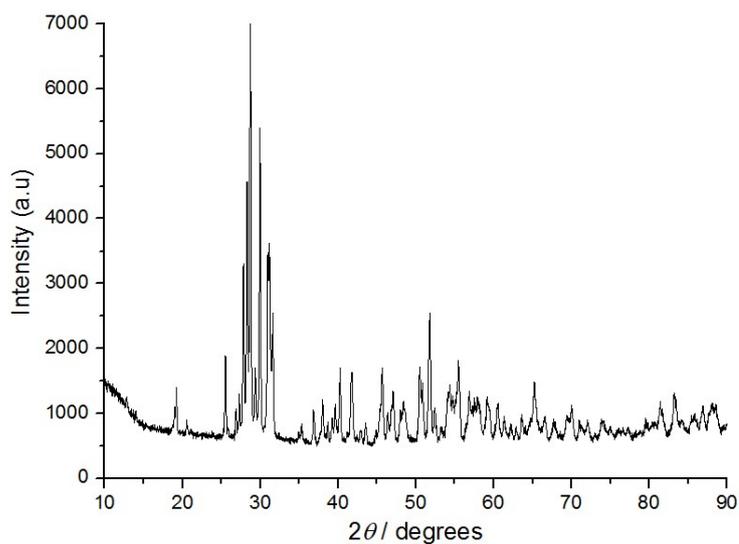


Figure S2-2: XRD pattern obtained in the 10-90° range for  $\text{Ca}_2\text{V}_2\text{O}_7$ .

The Raman spectrum of this compound (**Fig.S2-3**) is a very good concordance with that published by Occelli et al. <sup>2</sup>.

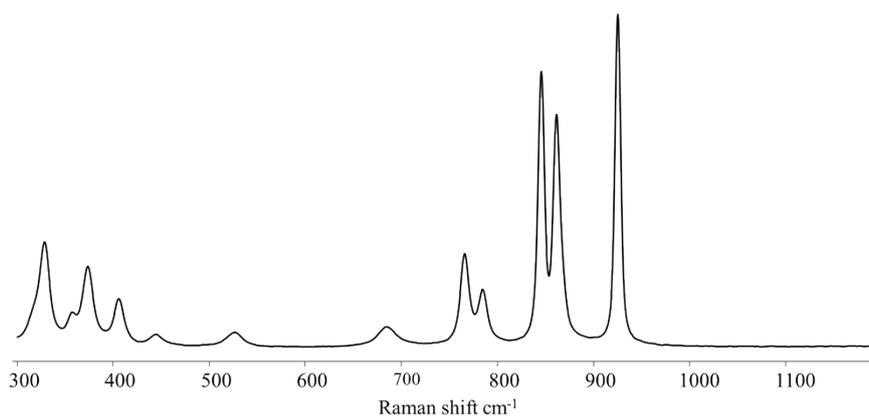


Figure S2-3: Raman spectra recorded in the 300-1200  $\text{cm}^{-1}$  range for the  $\text{Ca}_2\text{V}_2\text{O}_7$

## REFERENCES

1. X. Gao, P. Ruiz, Q. Xin, X. Guo and B. Delmon, *Catal. Lett.*, 1994, **23**, 321-337.
2. M. L. Occelli, R. S. Maxwell and H. Eckert, *Microp. Mesop. Mater.*, 1994, **3**, 305-318.