

Supplementary Information

Experimental and Analytical Methods

Experimental solutions made from diammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$, and sodium arsenate, Na_2HAsO_4 , (purchased from Sigma-Aldrich without further treatment) were reacted with gem quality calcite crystals crushed to 0.3-2 mm. Hydrothermal replacement experiments were conducted using a titanium cell with 13.5 ml internal volume and a flexible graphite o-ring.

For each experiment, approximately 0.2 g of calcite grains and 5 ml of solution were added to the cell, and placed in an oven at set temperature for the period of experimental time. Preliminary experiments at 180°C showed that the reaction slows down as temperature decreases, with almost no reaction at ambient temperature. All the data presented in this study were from experiments conducted at 250°C ($\pm 1.0^\circ\text{C}$).

After each experiment, the closed cell was cooled to room temperature rapidly using a desk fan. The reacted solids were filtered, washed repeatedly with distilled water then air dried. Electron microprobe analysis was used to understand the spatial distribution of elements in the product grains. A series of grains were mapped to explore spatial chemical heterogeneity and spot analyses used to confirm extremes of composition. Selected larger grains (~1-2mm) were mounted in an epoxy resin, then cut and polished back to their approximate center for microanalysis. The quantitative spot microanalysis, elemental mapping and cathodoluminescence spectroscopy were conducted using the JEOL 8500F-CL HyperProbe field-emission gun electron probe microanalyser (FEG-EPMA) at CSIRO laboratories, with accelerating voltage of 15 Kev. Elemental mapping was also performed using a Zeiss Ultra Plus FEG-SEM equipped with a Bruker eFlash EDX detector at the Australian Resources Research Centre.

A series of reactions, converting calcite to apatite with solution arsenic concentrations with molar ratios ($X_{\text{As}} = \text{As}/(\text{As}+\text{P})$) ranging from 0.01 – 0.15, were run for 48 hours to ensure complete replacement of calcite by As-bearing apatite. In addition, to explore if the composition of the reaction product, hydrothermally synthesized apatite, can be further modified, a partially reacted sample (sample 2-7, Fig. 1b) was reacted with pure sodium arsenate solution at 250°C.

For the fully reacted samples, finely crushed (<300 micron) solid samples prepared for bulk elemental analysis underwent digestion with bromine followed by aqua-regia. The digest solutions were then made to 50ml in 5% nitric acid. The Ca, Na, P and As content of the reacted products were analyzed using the ICP-OES method, where the uncertainty is typically on the order of 2%. Hydroxylapatite pattern were observed in x-ray powder

diffraction analysis. The $(\text{Na}+\text{Ca})/(\text{P} + \text{As})$ ratio of 2.0-2.15 in the Table S1 are consistent with theoretical P/Ca ratio of 2.16 of hydroxylapatite within analytical error.

Table DR1. ICP- analytical results of element composition in the fully reacted samples (theoretical composition of P and Ca in hydroxylapatite from molecular weight is 18.5% and 39.9%, respectively. $\text{Ca}/\text{P} = 2.16$)

SAMPLE ID	As (wt%)	Ca (wt%)	Na (wt%)	P (wt%)
R6-5	0.09	38.8	0.13	18
R6-6	0.25	39.1	0.21	18.3
R6-7	0.58	38.9	0.24	18.1
R6-8	1.31	38.1	0.34	17.9

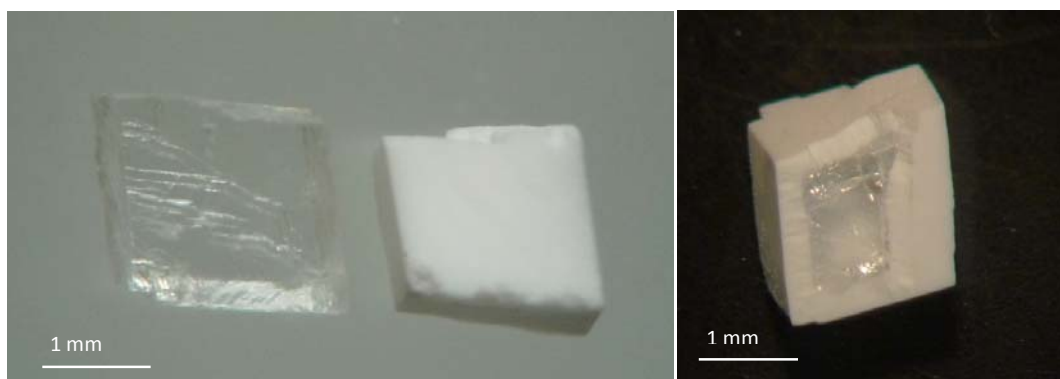


Figure DR1. a) Calcite crystal (left), and product after reacting calcite with a solution containing $(\text{NH}_4)_2\text{HPO}_4$ and Na_2HAsO_4 at 250 °C for 24 hours. b) Partially reacted grain showing the un-reacted calcite core and an apatite rim.