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Giant uranium deposits formed from exceptionally uranium-rich acidic brines

Antonin Richard^{1*}, Christophe Rozsypal¹, Julien Mercadier^{1†}, David A. Banks², Michel Cuney¹, Marie-Christine Boiron¹ and Michel Cathelineau¹

Giant uranium deposits were formed during the Mesoproterozoic era, 1.6–1.0 Gyr ago, in both Canada and Australia. The deposits are thought to have formed from large-scale circulation of brines at temperatures of 120–200 °C that percolated between sedimentary basins and underlying crystalline basement rocks^{1–3}. However, the precise conditions for transport of the uranium in these brines are poorly understood^{4–7}. Here we use mass spectrometry to analyse the uranium content of brines preserved in naturally occurring fluid inclusions in ore deposits from the Athabasca Basin, Canada. We measure concentrations of uranium in the range 1.0×10^{-6} – $2.8 \times 10^{-3} \text{ mol l}^{-1}$. These concentrations are three orders of magnitude above any other common crustal fluids. Experimentally, we measure the solubility of uranium as a function of NaCl content and pH, in mixtures that are analogous to ore-forming brines at 155 °C. To account for the high uranium content observed in the Athabasca deposits, we find that the brines must have been acidic, with a pH between 2.5 and 4.5. Our results strongly suggest that the world's richest uranium deposits formed from highly concentrated uranium-bearing acidic brines. We conclude that these conditions are a necessary requirement for the formation of giant uranium deposits in relatively short periods of time of about 0.1–1 Myr, similar to other world-class deposits of lead–zinc and gold^{8,9}.

Models for the formation of hydrothermal ore deposits imply either protracted fluid flow with relatively low metal concentration¹⁰, or more discrete pulses of extremely metal-rich fluids^{8,9}. The dynamics of metal input in the ore systems has profound consequences for the duration of mineralizing events, a crucial issue to ore genesis^{8–10}. If there is no possibility of acquiring sufficiently precise geochronological data, as in the present case¹, the duration of the mineralizing events is first-order approximated by (1) metal concentration in mineralizing fluids, (2) fluid-flow rates and (3) rates of precipitation of the metal-bearing minerals. Therefore, to understand massive metal transport and deposition in the Earth's crust, both analytical and experimental studies on deep fluids are needed^{8–14}.

Unconformity-related U deposits from the Proterozoic Athabasca (Canada) and Kombolgie (Australia) basins show spectacular grades and tonnages (up to 200 kt U and up to 20% U on average) when compared with the average U content of ~1 ppm in the continental crust¹⁵. They document the remarkable efficiency of the processes of U concentration from the source rocks to the UO₂ deposits¹. In these basins, the basal sandstones underwent large-scale circulation of evaporated seawater-derived oxidizing brines at a temperature of 120–200 °C (refs 16–18). These

25–35 wt% NaCl equivalent brines have percolated the Archean to Palaeoproterozoic crystalline basement, a potentially important U source¹⁹, during the reopening of ancient fractures²⁰.

In the vicinity of the studied U deposits, haematite is widespread and no magnetite is observed (Fig. 1; refs 1, 17). Therefore, the oxygen fugacity (f_{O_2}) in the system should have been above the haematite–magnetite buffer and the U should have been dissolved in the form of U(VI). Thermodynamic calculations have shown that $\log f_{\text{O}_2}$ must have been above –24 at 200 °C to account for $\sim 10^{-5} \text{ mol l}^{-1}$ of dissolved U(VI) (as uranyl complexes), well above the haematite–magnetite buffer ($\log f_{\text{O}_2} = -39.5$ at 200 °C; ref. 5). The reduction of U(VI) to U(IV) and subsequent UO₂ precipitation was spatially associated with the intersection of graphite- and sulphide-rich basement-rooted faults and the basement-cover unconformity, which may have acted as redox interfaces²¹. Although these giant deposits imply that such brines are capable of transporting huge quantities of U, no experimental data are available for U(VI) solubility in these conditions^{22,23}. The very first laser ablation inductively coupled plasma mass spectrometry analyses of fluid inclusions representing preserved aliquots of the ore-forming brines in the Athabasca Basin revealed unexpectedly high U contents⁷ ($\sim 10^{-6}$ to $\sim 2 \times 10^{-3} \text{ mol l}^{-1}$ U). However, the small number of available data coupled with the lack of experimental work prompted further study to confirm and understand these results.

Systematic analytical determination of the U concentration in natural fluid inclusions from four unconformity-related U deposits in the Athabasca Basin (Rabbit Lake, Eagle Point, P-Patch and Millennium) is reported here. Fluid inclusions were selected in quartz veins contemporaneous with major alteration events and ore deposition^{1,16,17} (Fig. 1). Because mineralized and barren samples host similar quartz veins and enclosed fluid inclusions¹⁷, only barren samples were selected to avoid contamination by tiny UO₂ solid inclusions in quartz which was frequently observed in some mineralized samples from McArthur River deposit⁷. Within mineralized and barren quartz veins, the petrography of fluid inclusions is generally complex owing to alternating quartz-growth and quartz-dissolution episodes and intense microfracturing during quartz growth leading to the formation of clusters of primary and pseudosecondary inclusions¹⁷. These processes are recurrent throughout the formation of millimetre-sized quartz, and primary and pseudosecondary inclusions could possibly be distinguished from each other only in some rare cases (Fig. 1). However, it is well established that late secondary inclusions are very scarce in these samples and that only 25–35 wt% NaCl equivalent brine inclusions are present¹⁷. Therefore, the analysed fluid inclusions are considered as representative of a single fluid event involved in quartz growth and transport

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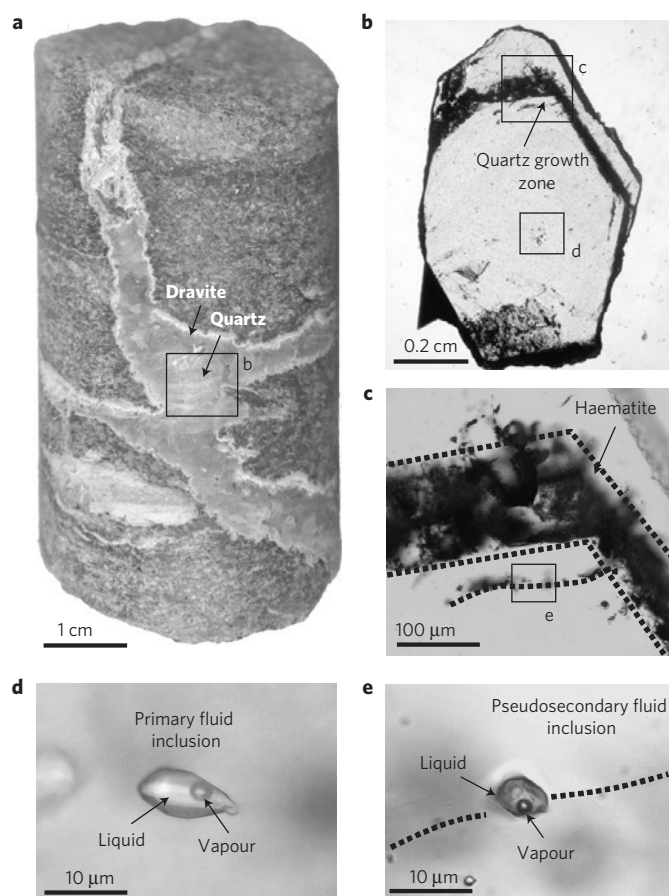


Figure 1 | Quartz-vein and fluid-inclusion petrography. **a**, Core sample showing a dravite (Mg-tourmaline)-quartz vein (typically associated with mineralizing events) crosscutting graphite-rich gneiss (sample H3042-1, Eagle Point deposit). **b**, Quartz wafer showing a well-identified growth zone. **c**, Magnification of growth zone characterized by abundant haematite (straight dashed lines). A pseudosecondary fluid-inclusion plane is indicated by the curved dashed line crosscutting the haematite-free quartz but not the latter haematite-rich quartz. **d**, Two-phase primary fluid inclusion. **e**, Two-phase pseudosecondary fluid inclusion. Such inclusions represent preserved aliquots of the ore-forming brines and were selected for LA-ICP-MS analysis.

of $U(vi)$. Fluid inclusions were analysed by microthermometry and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), which is at present the most accurate and sensitive technique for the determination of the major- and trace-element ratios within fluid inclusions^{24,25}, and provides absolute element concentrations when combined with the salinity determined from microthermometry (Methods and Supplementary Table S1).

The minimum U concentration required for LA-ICP-MS determination varies as a function of inclusion size and therefore of the signal intensity (here between $\sim 10^{-6}$ and $\sim 2 \times 10^{-4} \text{ mol l}^{-1}$ for large and small inclusions, and most frequently below $\sim 4 \times 10^{-6} \text{ mol l}^{-1}$). Of the 166 analysed fluid inclusions, 104 have measurable U concentrations, comprised between 10^{-6} and $2.8 \times 10^{-3} \text{ mol l}^{-1}$ and varying over three orders of magnitude in all the studied deposits (Fig. 2). Because the U concentrations are highly scattered, no statistically relevant relationship is evident between U content of fluid inclusions and a given deposit or sample. The range of U concentrations found here is consistent with the first measurements made at McArthur River⁷ and shows that the chlorine-rich brines were indeed U -bearing fluids, with the U content and variability being comparable from one

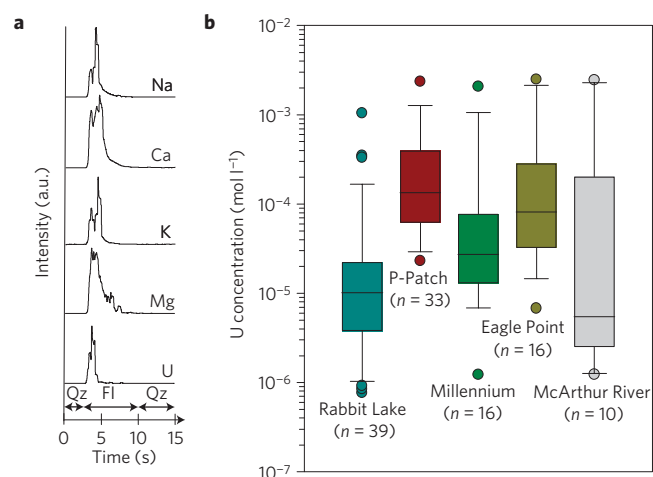


Figure 2 | LA-ICP-MS determination of U concentration in fluid inclusions. **a**, LA-ICP-MS signal for selected elements in a $1.0 \times 10^{-3} \text{ mol l}^{-1}$ U fluid inclusion (sample RBL1Qz, Rabbit Lake deposit). U is absent from quartz (Qz) and is entirely fluid-inclusion hosted as no U signal is observed during quartz ablation before opening of the fluid inclusion (FI). a.u., arbitrary units. **b**, Box-and-whisker plots showing the distribution of U concentration in fluid inclusions among the studied deposits. Lower whiskers, bottoms of boxes, central lines, tops of boxes and upper whiskers represent 10th, 25th, 50th, 75th and 90th percentiles respectively; symbols represent outliers. McArthur River data have been published previously⁷. n , number of fluid inclusions analysed.

sample to another and from one deposit to another throughout the Athabasca Basin.

An experimental determination of $U(vi)$ solubility as a function of $pH_{155^\circ C}$ (1.9 to 6.8) and $NaCl$ concentration (0.3 to 6.0 mol l^{-1}) in H_2O - $NaCl$ mixtures, an analogue of the ore-forming brines, was carried out by reacting an excess of solid hydrated uranium trioxide $UO_3(H_2O)_n$ in H_2O - $NaCl$ mixtures at $155^\circ C$ and P_{sat} in a polytetrafluoroethylene container placed in an autoclave under argon atmosphere (Methods and Supplementary Table S2). As polytetrafluoroethylene and argon are chemically inert in these conditions, this experimental set-up prevents the occurrence of any redox reaction and ensures that the U remains in the $U(vi)$ form. Once stabilized, the pH of each synthetic brine was measured at $25^\circ C$. The $pH_{155^\circ C}$ is reasonably assumed to be ~ 1 unit below $pH_{25^\circ C}$ irrespective of salinity, on the basis of the thermodynamic properties of aqueous $NaCl$ at $155^\circ C$ (refs 26,27).

The results of solubility measurements show that $U(vi)$ solubility lies between $\sim 10^{-7}$ and $\sim 10^{-5} \text{ mol l}^{-1}$ for $pH_{155^\circ C}$ between 4.5 and 6.8, but reaches $\sim 10^{-1} \text{ mol l}^{-1}$ at $pH_{155^\circ C} \sim 2$ (Fig. 3). For Na concentrations below 4.4 mol l^{-1} , the solubility of $U(vi)$ is not significantly dependent on the salinity. For samples with Na concentrations above 4.4 mol l^{-1} and $pH_{155^\circ C}$ below 4.3, the solubility of $U(vi)$ is down to two orders of magnitude lower than in samples with a lower Na concentration and a similar $pH_{155^\circ C}$. This decrease of $U(vi)$ solubility with increasing salinity is due to the precipitation of sodium uranates during the experiments, which were identified by Raman spectroscopy (Supplementary Fig. S1). However, the results of the experiments show that the pH is clearly the main control on $U(vi)$ solubility, especially in the most acidic media.

In the studied deposits, the pH of the ore-forming brines can be estimated using the activity diagram for the system HCl - H_2O -(Al_2O_3)- K_2O - SiO_2 showing $\log a_{K^+}/a_{H^+}$ versus $\log a_{H_4SiO_4}$ (where a is the activity) at $150^\circ C$ (ref. 28; Supplementary Fig. S2). Considering that the brines lie in the field of stability of illite⁶, along the quartz saturation line¹⁷ and close

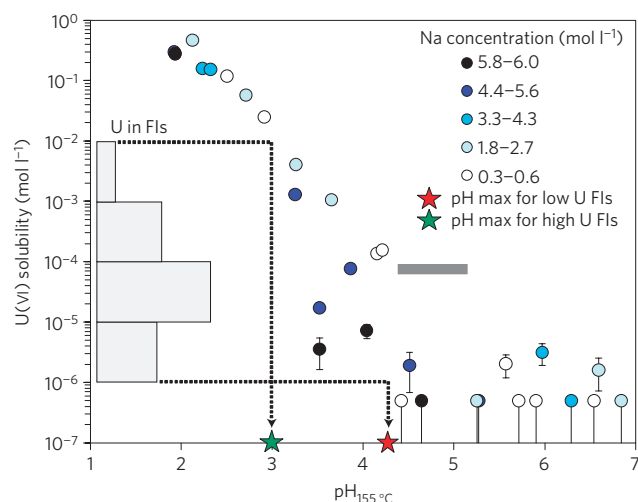


Figure 3 | U(VI) solubility in H₂O–NaCl mixtures at 155 °C and P_{sat} as a function of $\text{pH}_{155\text{ °C}}$ and Na concentration. The distribution of U concentration in fluid inclusions (FIs) is reported in the histogram. Matching fluid-inclusion and experimental data indicates that the pH of the ore-forming brines was between 2.5 and 4.5 (see text for explanations). Error bars reflect the analytical uncertainty on U(VI) solubility. Downward vertical bars indicate that the plotted value is the limit of detection for U(VI) ($5 \times 10^{-7} \text{ mol l}^{-1}$) when U was not detected in synthetic brines. Grey bar, hydrochemical and thermodynamic modelling of the ore-forming brines^{4,5}.

to the stability field of kaolinite¹⁶, with K concentration between $\sim 10^3$ and $\sim 3 \times 10^4$ ppm (Supplementary Table S1), the pH would approximately range from 2.5 to 4.5.

As chloride is by far the dominant anion in the natural¹⁸ and synthetic brines studied here, it is reasonable to assume that the U complexation is similar in the two cases. No U(VI) minerals have been found in the studied deposits, and therefore the ore-forming brines were undersaturated with respect to U(VI) minerals, in contrast to the high-salinity synthetic brines, which were saturated with respect to sodium uranates (Supplementary Fig. S1). As a consequence, the maximum possible pH value of the ore-forming brine enclosed in one fluid inclusion can be deduced from its salinity and U concentration (Fig. 3). Considering the whole range of measured U concentrations in fluid inclusions, a range of 2.5–4.5 can be considered as reasonable for the pH of the ore-forming brines (Fig. 3), which is compatible with that found independently using the activity diagram (see above).

The estimated pH values are far lower than previously thought in this context^{5,6} and unusually low for geological fluids, especially in the absence of H₂S or organic acids. One possible explanation is that such low pH was acquired by sulphide oxidation at surface or near-surface conditions in evaporitic environments from which the ore-forming brines originated^{18,29}. Although the origin of acidity in the studied brines remains to be better understood, it seems that their low pH is a key factor contributing to the high U concentrations.

The observed variability of U concentrations in fluid inclusions at the sample scale is best explained by (1) variations in the pH of the brines in the 2.5–4.5 range controlling the maximal concentration of U dissolved in the proximal source rocks and/or (2) ongoing UO₂ precipitation resulting in the differentiation between pre-ore brines (that is, U rich) and spent-ore brines (that is, U depleted). Both scenarios would result in spatial and temporal heterogeneity of U concentration in the brines and high variability of U concentrations in fluid inclusions at the sample scale. Contamination by tiny U-bearing solids accidentally trapped during the formation of fluid inclusions is ruled out because U-bearing solids in fluid inclusions of such high U content would be optically visible³⁰ and a detailed

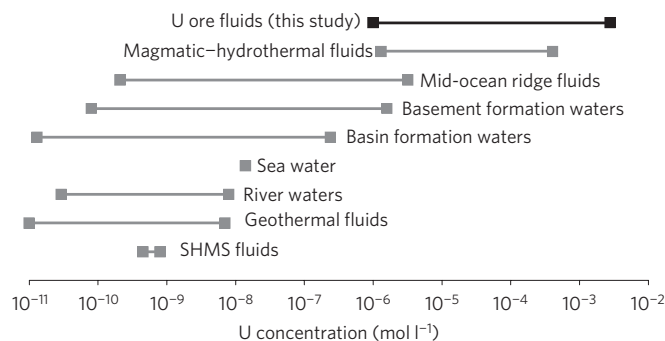


Figure 4 | Comparison of U concentrations in Athabasca U ore fluids (this study) with U concentration in various crustal fluids. Most crustal fluids have U concentrations below $10^{-6} \text{ mol l}^{-1}$ except for fluids related to the magmatic-hydrothermal activity around granitic intrusions ($T > 400\text{ °C}$), and U ore fluids (this study), which have U concentrations up to three orders of magnitude above any other geological fluids. Full references, U concentrations, temperature, pH and salinity data for the fluids shown here are provided in Supplementary Table S3. SHMS fluids, sedimentary-hosted massive sulphide mineral deposit fluids.

Raman spectroscopy analysis of fluid inclusions from McArthur River deposit has not revealed any U-bearing solid¹⁷.

High U concentrations comparable to those measured in the studied fluid inclusions and synthetic brines ($\sim 10^{-6}$ to $\sim 10^{-3} \text{ mol l}^{-1}$) have previously only been measured in very high-temperature (above 400 °C), high-salinity (above 40 weight% NaCl equivalent) and acidic magmatic-hydrothermal fluids (Fig. 4 and Supplementary Table S3). U concentrations in basin and basement formation waters, geothermal fluids and mid-ocean ridge fluids rarely exceed $10^{-6} \text{ mol l}^{-1}$. Therefore, the studied fluids are exceptionally U rich when compared with other crustal fluids for which the temperature is lower than 400 °C , and other crustal fluids with comparable low pH do not carry such quantities of U (Supplementary Table S3). From this, we conclude that the studied brines have such exceptional U content first because of their high f_{O_2} , second because of the high U availability in the environment of the deposits¹⁹ and last because of their rather unusually low pH, which enables the U to remain stable in solution.

Using a flow rate of $\sim 1 \text{ myr}^{-1}$, a U concentration of $\sim 10^{-4} \text{ mol l}^{-1}$ in the ore forming brines is required to form such deposits in a geologically reasonable period of time (~ 0.1 – 1 Myr ; ref. 4). Here, we demonstrate that $\sim 10^{-4} \text{ mol l}^{-1}$ U in the ore-forming brines averages the concentrations found in fluid inclusions (Fig. 3). Therefore, a first-order approximation confirms that 0.1–1 Myr is a viable estimate for the duration of the mineralizing event.

More generally, the hypothesis that world-class lead–zinc and gold hydrothermal deposits are produced by exceptionally metal-rich fluids in a relatively short period of time^{8,9} can also be extended to giant unconformity-related U deposits. Such a conclusion could be reasonably extrapolated to other types of high-grade large-tonnage metal deposit, provided a comprehensive analytical and experimental investigation of ore fluid metal contents.

Methods

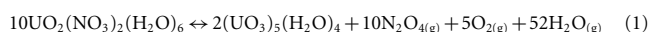
Fluid-inclusion microthermometry was carried out using a Linkam MDS600 heating-cooling stage using the procedure and fluid-inclusion nomenclature previously published for fluid inclusions in the Athabasca Basin^{7,17}.

LA-ICP-MS analysis of fluid inclusions from nine quartz vein samples was carried out at the School of Earth and Environment, University of Leeds, UK, using published instrumentation and procedures²⁵. Calibration and signal integration were carried out with the MATLAB-based SILLS program^{31,32}. The limit of detection was defined as 3σ error above the blank. Absolute element concentrations can be calculated if the Na internal standard concentration is known. The Na concentration was obtained from the chlorine content determined

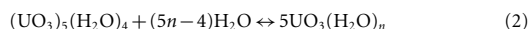
by microthermometry and the analysed elemental ratios to Na using the charge-balance technique²⁵. On the basis of microthermometric measurements, a deduced chlorinity of 6.5 mol kg⁻¹ was attributed to all inclusions, which may over- or underestimate absolute concentrations by a maximum of 15% relative, but more generally around 10% (ref. 17). Fluid-inclusion assemblages containing chlorine-rich brine inclusions were selected and 166 fluid inclusions devoid of any visible solids (except halite) were ablated. A summary of LA-ICP-MS data is shown in Supplementary Table S1.

The experimental determination of the solubility of U(vi) in synthetic NaCl brines (0.3–6.0 M) as a function of pH (1.9–6.8) at 155 °C and vapour saturation pressure was established as follows. The U was provided by Fluka as uranyl nitrate hexahydrate UO₂(NO₃)₂(H₂O)₆. The hydrochloric acid was provided by Riedel de Haen as a HCl–H₂O mixture saturated with HCl (37% by mass). The sodium hydroxide was provided by Baker as sealed phials containing 6.67 mol of NaOH per litre of NaOH–H₂O mixture and by Prolabo in the form of NaOH solid pellets, the latter being used for the preparation of NaOH–H₂O mixtures requiring a NaOH concentration higher than 6.67 mol l⁻¹. The water we used was distilled water with a resistance over length of 18.2 MΩ cm⁻¹. The argon was provided by Air Products. Hydrated uranium trioxide (UO₃)₅(H₂O)₄ was prepared, according to reaction (1), by heating the uranyl nitrate hexahydrate at 300 °C (ref. 33). The obtained (UO₃)₅(H₂O)₄ was then heated, in the presence of distilled water, in an autoclave at 155 °C under saturation vapour pressure, according to reaction (2).

At 300 °C:



At 155 °C:



HCl–H₂O mixtures, containing from 1 to 12 mol of HCl per litre, were prepared by diluting concentrated hydrochloric acid in distilled water. NaOH–H₂O mixtures with the same concentrations were prepared by dissolving solid NaOH pellets in distilled water for those with a NaOH concentration higher than 6.67 mol l⁻¹ or by diluting the Baker product for those with lower concentrations. Aqueous NaCl media at a concentration of N mol l⁻¹ NaCl were prepared by mixing 2N HCl–H₂O and 2N NaOH–H₂O mixtures in equal proportions. The pH of these media was adjusted to values between 2.9 and 8 with HCl at 2N mol l⁻¹ or NaOH at 2N mol l⁻¹ so as to neither modify the ionic strength of the media nor add other chemicals. 30 media were prepared using this procedure with N ranging from 0.35 to 5.94. 500 mg of UO₃(H₂O)_n were introduced in 15 ml of each prepared NaCl medium. Each obtained sample was placed in a 20 ml polytetrafluoroethylene container, which was in turn placed in an autoclave, and heated at 155 °C under saturation vapour pressure. After two weeks, each autoclave was extracted, quickly cooled by water quenching, and opened under an argon atmosphere. The pH of the samples was measured with a Ross electrode and corrected for Na ion interferences thanks to a table provided with the electrode. If different from its initial value after correction, the pH was readjusted to this value with the corresponding HCl–H₂O or NaOH–H₂O mixture. The samples were again placed in the autoclave and heated at 155 °C for two weeks and the procedure repeated until the pH remained stable. The duration of the experiments was approximately 4 months in the acidic media and up to 6 months in the neutral ones. When the pH had stabilized, the extracted samples were filtered in a 220 nm filtration column to separate the liquid phase from the solid phase. The liquid phases were analysed for U and Na concentration by ICP–atomic emission spectroscopy at Laboratoire de Chimie Physique et Microbiologie pour l'Environnement (LCPME; Nancy, France) using a Jobin-Yvon Ultima argon spectrometer. The targeted wavelengths were 588.995 nm for sodium and 385.958 nm for U. The limit of detection for U was 5 × 10⁻⁷ mol l⁻¹. The solid phases were analysed by backscattering Raman spectroscopy at LCPME (Nancy, France) using a Jobin-Yvon Spex spectrometer with a He–Ne laser beam with an excitation wavelength of 632.8 nm. Three measurements, lasting 40 s each, were conducted for each solid phase.

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Author contributions

M. Cuney, M. Cathelineau and M.-C.B. conceived the project. J.M., M. Cathelineau and M. Cuney collected samples used in this study. A.R., M.-C.B. and J.M. did the petrographic and microthermometric analyses of fluid inclusions. D.A.B., A.R. and M.-C.B. carried out the LA–ICP–MS analyses of fluid inclusions. C.R. did the experimental U solubility measurements and analyses. A.R. and C.R. wrote the manuscript with contributions from all co-authors. All co-authors contributed to the discussion and interpretation of the data.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at <http://www.nature.com/reprints>. Correspondence and requests for materials should be addressed to A.R.