Supplementary Material 1: Analytical Methods, Electron Probe Microanalysis

Quantitative compositions of REE-fluorocarbonates were determined using a Cameca SX-Five electron probe microanalyzer (EPMA) equipped with 5 tunable wavelength-dispersive spectrometers. The microscope uses PeakSite software for microscope operation, and Probe for EPMA software (distributed by Probe Software Inc.) for data acquisition and processing. The REE-fluorocarbonate structure is able to substitute a diverse range of elements at highly variable concentrations. As such it was necessary to analyze for a large list of elements at variable operating conditions to minimize any dead time and beam damage effects. For major to minor elements operating conditions were 15 keV/20nA, with trace elements acquired at an increased beam current of 100 nA (see supplementary Table S2).

Initially, a set of 42 elements was measured F (Kα), Na (Kα), Mg (Kα), Al (Kα), Si (Kα), P (Kα), S (Kα), Cl (Kα), K (Kα), Ca (Kα), Sc (Kα), Ti (Kα), V (Kα), Mn (Kα), Fe (Kα), Cu (Kα), As (Lα), Sr (Lα), Y (Lα), Zr (Lα), Nb (Lα), Te (Lα), Ba (Lα), Ta (Lα), W (Lα), Pb (Mβ), Bi (Mα), La (Lα), Ce (Lα), Pr (Lβ), Nd (Lβ), Sm (Lβ), Eu (Lα), Gd (Lβ), Tb (Lα), Dy (Lα), Ho (Lβ), Er (Lα), Tm (Lα), Yb (Lα), Th (Mα), and U (Mβ). This list was subsequently shortened by elimination of Mg, Sc, Ti, V, Mn, Cu, Te, Ba, Ta, and W since concentrations of these elements were consistently below minimum limits of detection (mdl). Detailed wave-scans were acquired on standards and unknowns to best determine positions for background measurements of these elements. A combination of traditional 2-point linear, multipoint fits, and "shared" background fits were used across the list of elements. In simple background regions, a traditional 2-point linear fit was used. For more complex regions of the spectrum, more background points are required, in which multipoint or "shared" fits were used [1-3]. Calibration and data reduction was carried out in Probe for EPMA, distributed by Probe Software Inc.

Mindful of the extended element list and beam damage effects, on-peak count times were 15-20 s for elements which are not the primary focus of this study (i.e. non-target elements) (Cu, Fe, Si, and others), 20-40 s for target elements (REE, Sr, and others), and 60-100 s for trace elements of interest (including Pb, U, and Th). Total acquisition time per analytical point was ~20 minutes. In addition, elements that are traditionally seen as "mobile" under the electron beam were analyzed first within the first 2 minutes of analysis, and include Na, F, Ca, K, P, and S.

The primary calibration and interference standards used in the analysis were of both synthetic and natural, and include the Smithsonian and Edinburgh REE, Astimex, P&H, and Taylor standard sets. Full detail of set up and standards can be found in supplementary Tables S2 and S3.

Supplementary Material 1 References

1. Goemann, K.; Donovan, J.J.; Feig, S.T.; Thompson, J. "Sharing" Background Measurements in Wavelength Dispersive Electron Probe Microanalysis. In: *Program Guide with Abstracts,* Microanalysis Society - Topical Conference on Electron-Probe Microanalysis, Madison, WI, USA, 16-19 May 2016; 28-29. ISBN 978-1-5323-0217-6.
2. Goemann, K.; Donovan, J.J.; Feig, S.T.; Thompson, J. Shared backgrounds in wavelength-dispersive electron probe microanalysis. In: *Book of Tutorials and Abstracts*, 15th European Workshop on Modern Developments and Applications in Microbeam Analysis, 7th Meeting of the International Union of Microbeam Analysis Societies, Konstanz, Germany, 7-11 May 2017; *European Microbeam Analysis Society eV*, 378-379. ISBN 978-90-8827-693-0.
3. Goemann, K.; Donovan, J.J. Electron probe microanalysis of complex natural sulphides using shared background measurements. In: *The Australian Microscopy & Micronalysis Society AMAS 2017*, 14th Biennial Australian Microbeam Analysis Symposium, Brisbane, Australia, 6-10 February 2017; 61-62. ISBN 978-0-9580408-6-0.