Residue from incomplete dissolution

Element	Average difference	Median difference
Li	-1%	0%
Be	-1%	0%
Ti	-2%	-1%
V	0%	0%
Cr	-1%	0%
Co	0%	0%
Ni	-4%	0%
Cu	4%	0%
Zn	-1%	0%
Ga	-5%	0%
Rb	0%	0%
Sr	-2%	0%
Y	-2%	-2%
Zr	0%	0%
Nb	-3%	0%
Mo	7%	1%
Sn	6%	3%
Cs	2%	1%
Ba	1%	1%
La	1%	0%
Ce	1%	0%
Pr	1%	1%
Nd	1%	0%
Sm	1%	0%
Eu	-1%	0%
Gd	1%	0%
Tb	0%	0%
Dy	0%	0%
Ho	0%	0%
Er	0%	0%
Tm	-1%	0%
Yb	-1%	0%
Lu	-1%	0%
Hf	0%	0%
Ta	-12%	0%
Pb	3%	0%
Th	4%	0%
U	2%	0%

There were some failures during experiments to develop an effective digestion procedure for metamorphosed (mostly) mafic and felsic igneous rocks that I work with. In two experiments the rock samples were not completely dissolved at the end. The undissolved material appeared as small amounts of white sludge at the bottoms of the vessels.

The sludge was essentially insoluble in water, so I washed it in DI water, then dissolved it in some dilute nitric acid (it dissolves slowly). Ion chromatograph and ICP-MS analysis demonstrated that these were aluminum-magnesium-calcium fluorides, as expected. Small quantities of the elements Li, Ti, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Sn, Cs, Ba, lanthanides, Hf, Pb, Th, and U were also found in the sludge. The other analyzed trace elements, Be, V, Nb, Mo, Rh, In, Ta, Re, and Bi were not found in the sludge. Note that Rh, In, Re, and Bi were added as internal standards.

X-ray diffraction was done on the washed sludge, but I found no convincing matches among any combinations of Al, Mg, Ca, F, Ti, O, and H_2O compounds in our mineral and inorganic diffraction powder diffraction file database.

40 samples were analyzed by ICP-MS using sludge-producing experimental procedures, and later were re-analyzed using the current non-sludgy procedure. For all 40 analysis pairs, the average and median relative deviations were calculated for each element (table). Negative numbers mean the sludgy samples had generally less of the element in solution, and presumably more in the sludge.

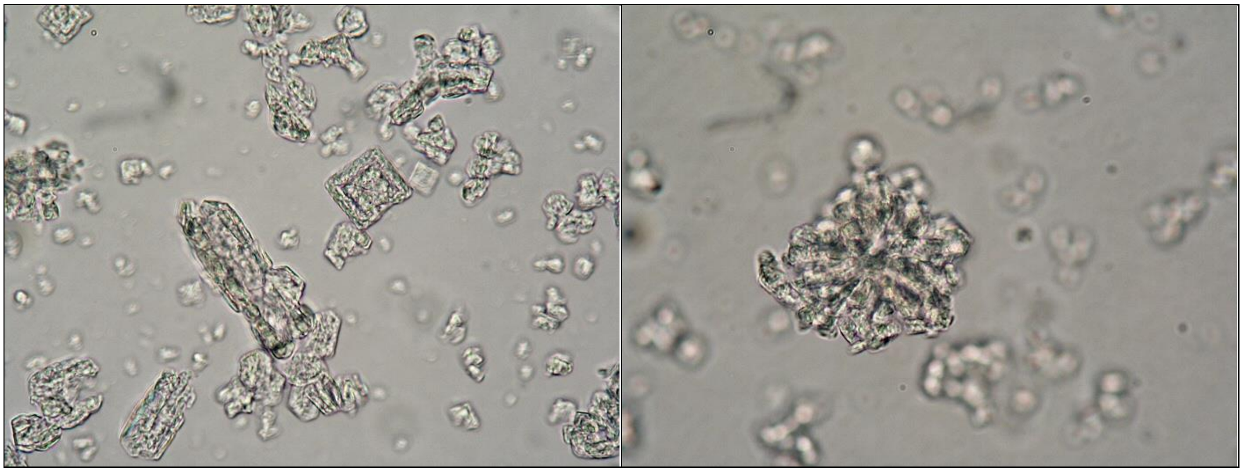
The bottom line is that having undissolved fluoride sludge in the bottom of the digestion vessels is not an analytical disaster, at least for these elements in these types of samples. Keep and use the analytical data until you can rerun the samples. Please forgive the average value for Ta and a few other elements; most of these samples were metamorphosed N-MORB cumulate gabbros, and Ta and some other elements had extremely low concentrations.

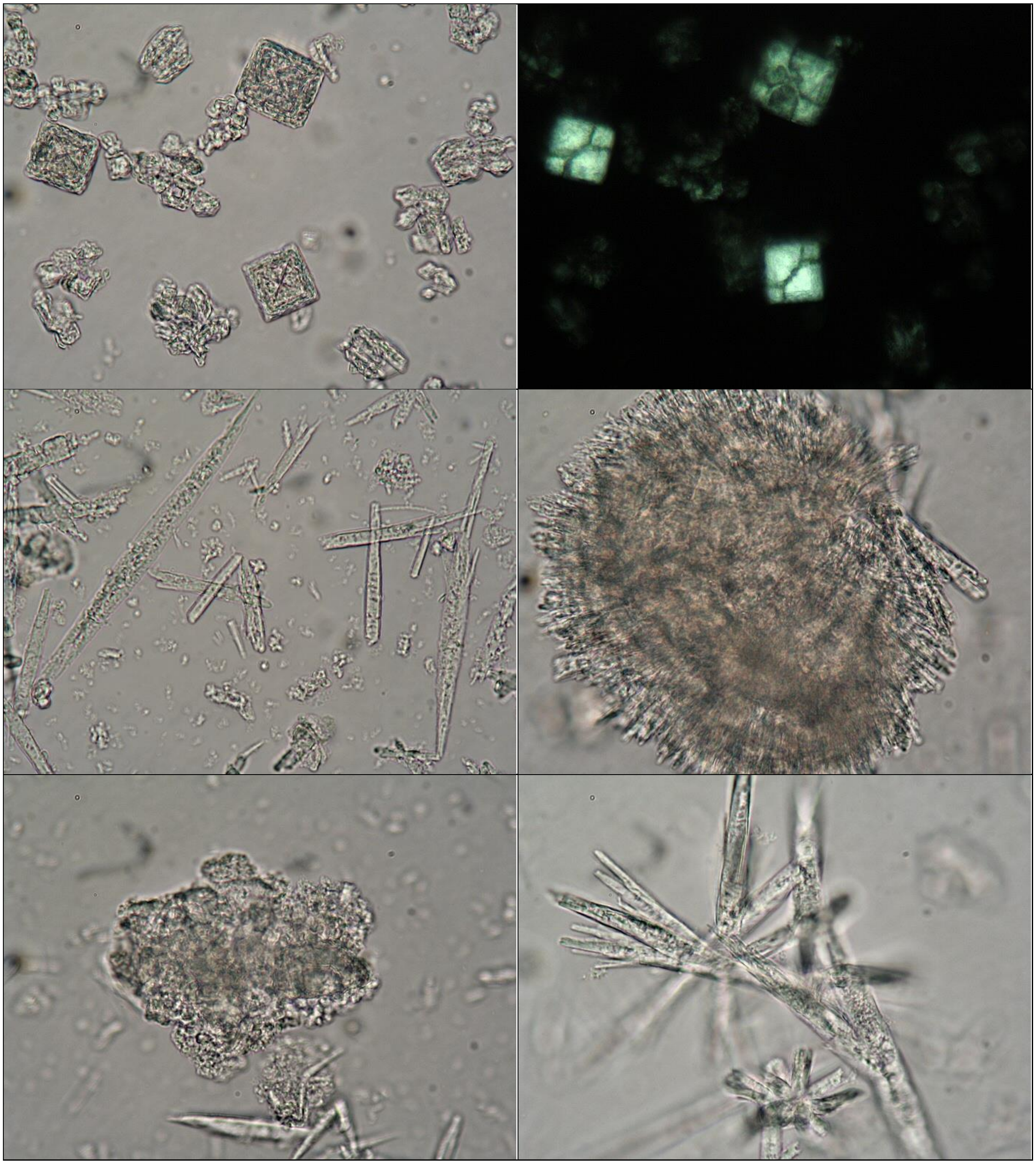
I suspect the reason that sludge formation made so little difference to the element concentrations is that there isn't any sludge when the solutions are pipetted for analysis. In all cases this was done within two hours of cooling the vessels from 150°C to room temperature.

Think of it this way. The sludge takes a long time to redissolve in nitric acid. I took ~10 mg of the sludge and suspended it in 45 ml of 20% HNO3 in a transparent plastic test tube. After two days at room temperature, with occasional shaking, it was still there and apparently unchanged. I put the test tube on its side in an oven at 50°C. Over a week it gradually vanished, leaving no residue. The dissolution rate is therefore very slow, so perhaps precipitation was also slow. My guess is that the sludge didn't even exist in significant amounts when the analyzed solutions were pipetted, but it formed over the next five days, which is when I looked for the sludge. In addition, the small quantities of elements released from dissolving sludge may have been in fluid inclusions. Because the fluid inclusions are trapped acid solution, they would not affect the concentration of elements in the rest of the solution.

As mentioned elsewhere, this procedure works fine for rocks with up to 6% TiO_2 (12 mg total, assuming 200 mg of sample), as determined by the lack of residue after dissolution, and by comparison of over 600 samples analyzed for TiO_2 in my lab and also at a commercial lab using lithium borate fusion and ICP-OES spectroscopy. However, I have also analyzed rutile and titanite mineral separates (chunks 1-2 mm across) and found that some white titanium residue was left. The rutile and titanite were completely decomposed, however, leaving a pure-white powder, so recoveries of other elements are probably close to 100%. For TiO_2-rich samples, modify this procedure by using less sample or more HF in the final dissolution step. Don't dissolve your sample introduction system, though.

For your edification, here are some photomicrographs of washed sludges from different samples. All photos have field widths of ~0.3 mm. There seem to be three main crystal shapes: cubes, needles, and elongated blocks. The proportions vary between different samples, presumably because of varying amounts of Al, Mg, and Ca in the original samples. Some photos are in cross-polarized light, showing crystals with no or low birefringence.





No picture.