

Problems in microwave digestion of high-Si and high-Al rocks

The microwave (MW) digestion of silicate rock samples has decided advantages over conventional open-vessel digestion techniques. Most obvious among these is the check on evaporation loss as the samples are digested in closed TEFLON vessels, and the second is the more efficient dissolution achieved due to increased vapour pressure in a relatively small time. Although quick and efficient, MW digestion is not totally a foolproof method that an analyst could use with complacency. During a year-long practice of digesting various rock types using the MW technique, we observed discrepancies in the Inductively Coupled Plasma-Atomic Emission Spectroscopic (ICP-AES) analysis of particularly Al in high-alumina samples. Here we have tried to track down the sources of such discrepancies and propose remedial measures to obtain the best estimates of the sample composition.

In order that the total number of steps are constrained to the barest minimum, we preferred neutralization of HF, residual from the silicate digestion step by addition of 4% boric acid solution so that Si is simultaneously analysed along with other major (Ti, Al, Fe, Mn, Mg, Ca, Na, K) and trace elements (Ba, Sr, Ni, Cr, Cu, Zn, V, Y and Zr) from the same solution. Non-neutralization of HF in the sample solution would harm the glassware used in sample nebulization, spray chamber and plasma torch assembly of the ICP instrumentation. We have followed here a modified version, detailed below, of the closed bomb digestion method¹ using a CEM MARS MW digestion system.

Accurately weighed 0.2 g of sample powder less than 200-mesh was placed in TEFLON vessels. Next, 5 ml of MilliQ water, 2 ml of concentrated aqua regia and 3 ml of concentrated HF were added

in the stated order and digested for 45 min at 200°C in the MW oven. After cooling to room temperature, an extra 10 ml of 4% boric acid was added and the digestion process repeated for an extra 15 min at 200°C. Following the final cooling the sample solution was poured into wide-mouthed polypropylene sample bottles of 120 ml capacity repeatedly rinsing with 4% boric acid. Exactly 40 ml of boric acid was used for rinsing. The cumulative volume of the resulting solution should not exceed 100 ml. Then the sample bottles were shaken for 15 to 20 min on an automatic shaker and the volume made to 100 ml with MilliQ water. Alternatively, the solution should be vigorously stirred for 5 min prior to the final dilution. This step is required to facilitate the rather slow complexation process of active HF in the solution with boric acid. In order to avoid contamination by reaction of active

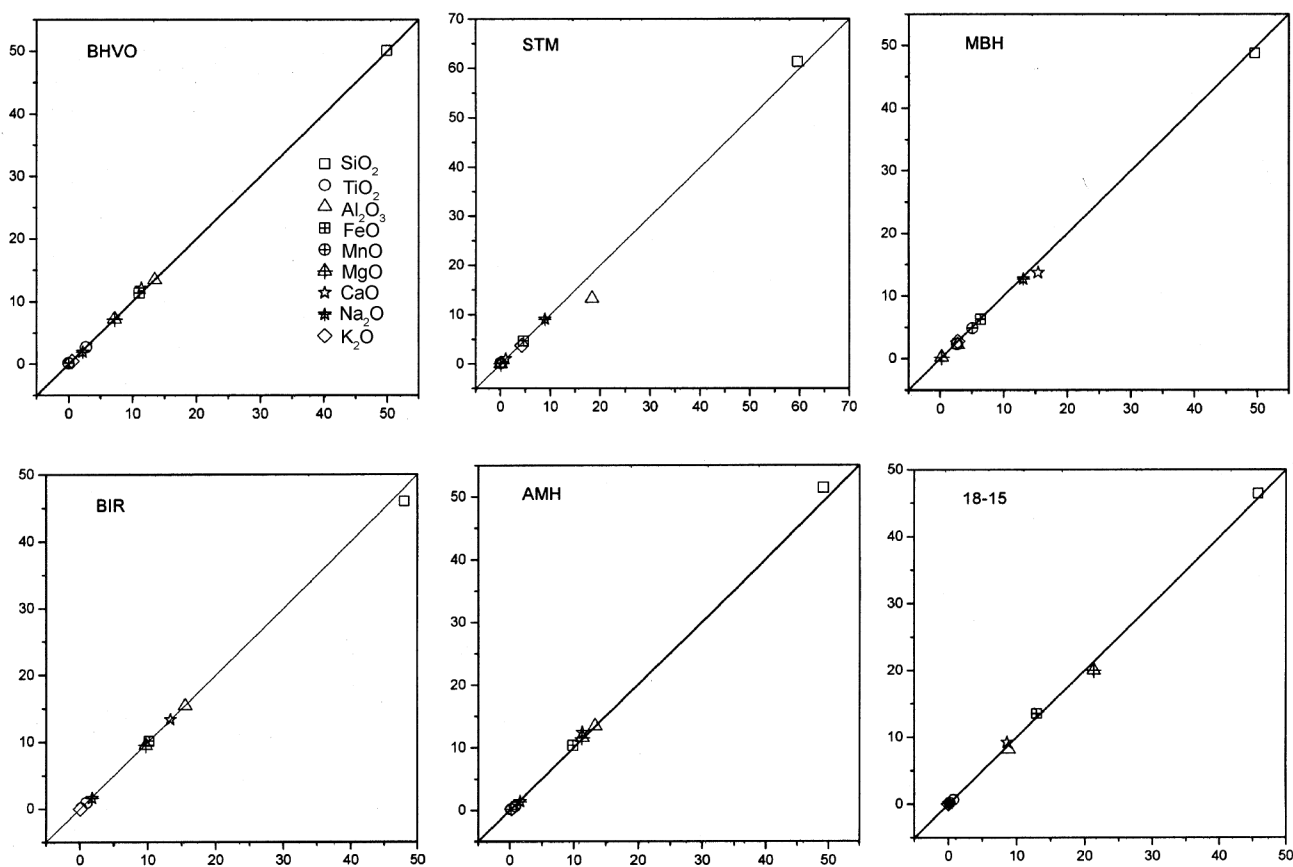


Figure 1. Plot of ICP major oxide analyses (in %) against respective standard values. Sample 18-15 is an in-house standard which was analysed separately by XRF. BHVO, BIR and STM are US Geological Survey standards, while AMH and MBH are standards from Wadia Institute of Himalayan Geology, Dehradun⁵. Notice that only Si and Al fall-off the equilines in some samples.

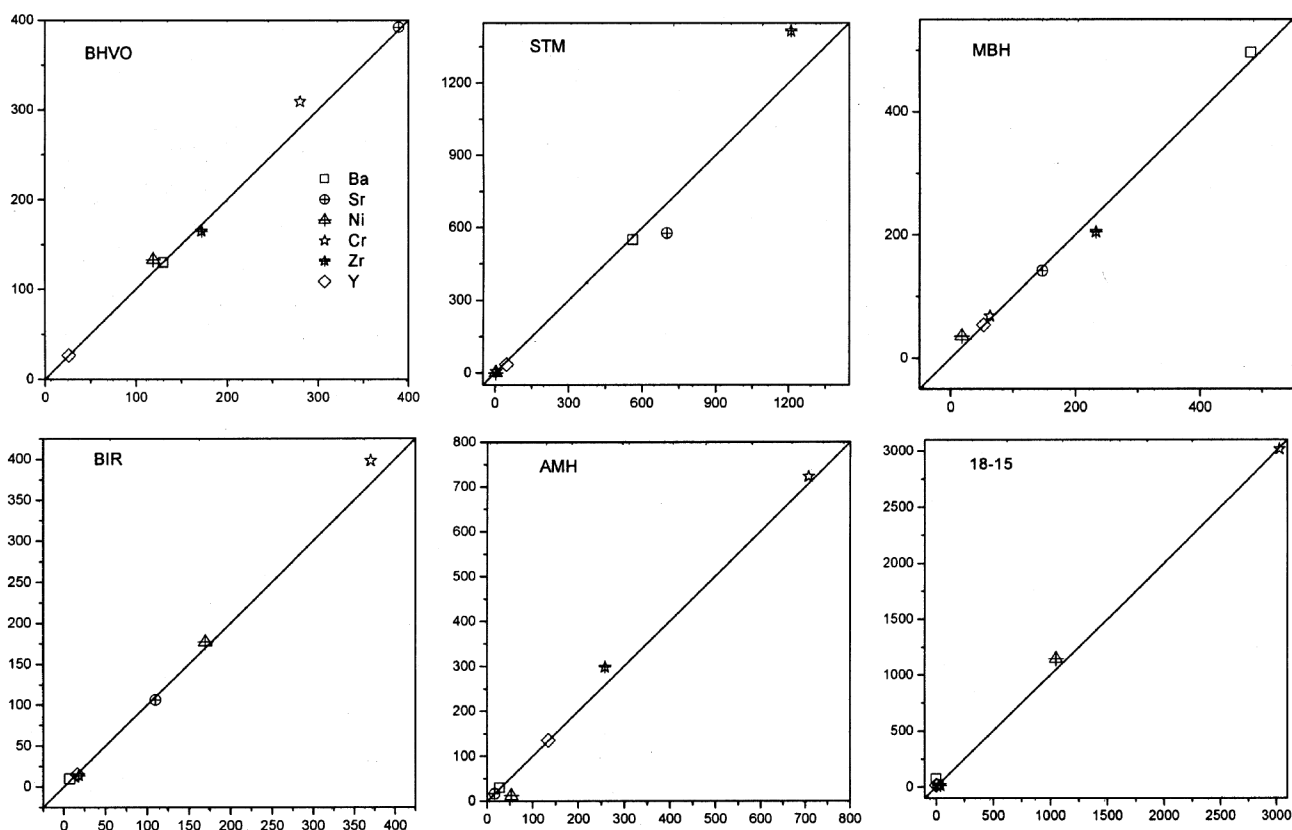


Figure 2. Estimated concentrations (in ppm) of selected trace elements plotted against standards. Except for Zr in STM, the errors are within acceptable limits.

HF with glass, the solution was stored in the polypropylene bottles. At least a day should be allowed before analysis.

The advantages are: (1) There is complete digestion of the sample without any evaporative loss. In case of refractory mineral-rich samples where complete digestion is not possible, the residue should be digested using a suitable fusion technique and separately analysed. Final result can be obtained by taking weighted average of the two. However, for most samples, separate fusion digestion is not required. (2) At a time a maximum of 12 samples can be processed saving considerable digestion time. The amount of acid consumed per sample is minimal compared to the conventional B-solution method². Less electricity is consumed as long drying processes on hot plates are done away with. (3) There is no emission of hot acid vapours minimizing health risks and the need for fume hoods is eliminated. (4) Major and trace elements can be analysed from the same solution without further dilution, thus minimizing systematic error during serial dilution. Because the MW technique is capable of breaking down

the refractory phases, elements like Zr, which are solely hosted in the refractory phases, can be analysed. (5) The biggest advantage of the boric acid complexation method is that Si can be analysed from the same solution, saving a lot of extra labour and time.

The accuracy of the technique can be evaluated from the comparative analyses of major oxides (Figure 1) and trace elements (Figure 2). All analyses were performed with ULTIMA-2 ICP-AES from Jobin-Yvon, France.

We encountered small but significant underestimation of Si and Al contents that mysteriously did not appear in all samples. Quartz-rich sand samples and pure quartz dissolve completely and give a composition of 99 to 100% SiO₂. The behaviour of a single control sample sometimes was completely unpredictable from one trial to another. Systematic observation over a prolonged period showed that only samples with high silica containing Al gave inconsistent analyses of both Si and Al. Standard sample solutions analysed after several months of storage did not show any discrepancy, providing a clue that

probably some precipitates formed metastably, which re-dissolved but with a slow rate. We observed the solutions for precipitated phases and found minor and fine accumulation at the bottom of some sample bottles, which was not there just after digestion. These precipitates generally appear in 12 to 24 h. Addition of a few millilitres of conc. HNO₃ suffices to re-dissolve these precipitates. Precipitation of pyrophyllite or kaolinite from the solution is probably the culprit. As shown in Figure 3, this problem can be circumvented by further diluting the solution so that the activity of silicic acid is lowered and precipitation of pyrophyllite or kaolinite is checked. Notice however that if there is precipitation of gibbsite this treatment will not be of help, as gibbsite stability is independent of the activity of silicic acid as also of the SiO₂ content. However, gibbsite precipitation most probably does not occur as the solution pH is invariably less than 3.

Samples with higher alumina but relatively lower silica do not behave in the way just described. Analyses of such samples are deficient in Al, but not so in

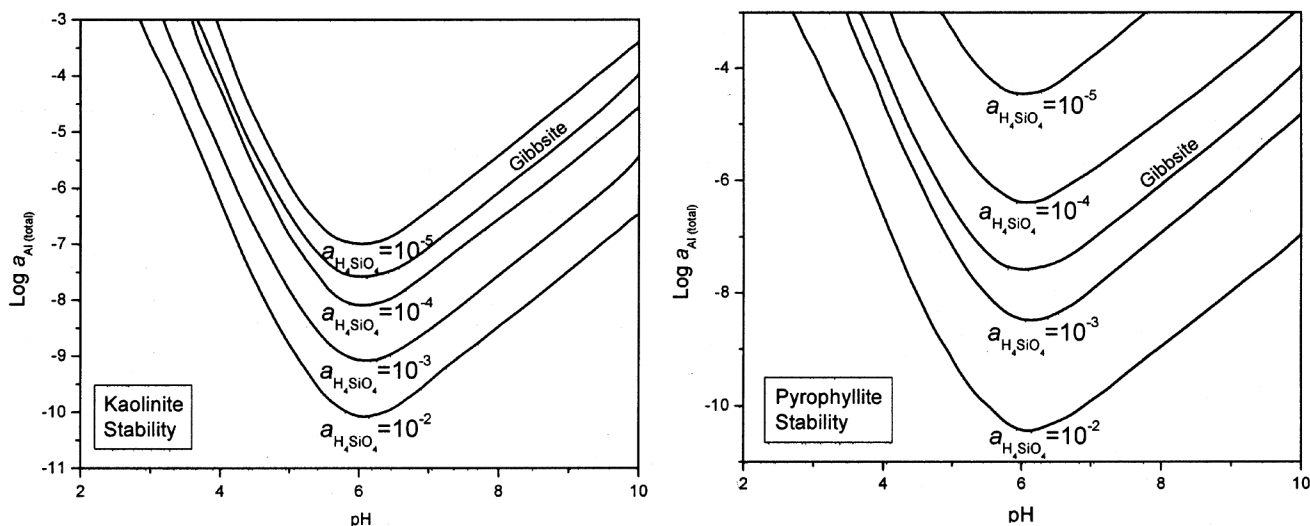


Figure 3. Stability of kaolinite and pyrophyllite as a function of activities of Al and H_4SiO_4 and of pH in aqueous solutions, adapted from Drever⁶.

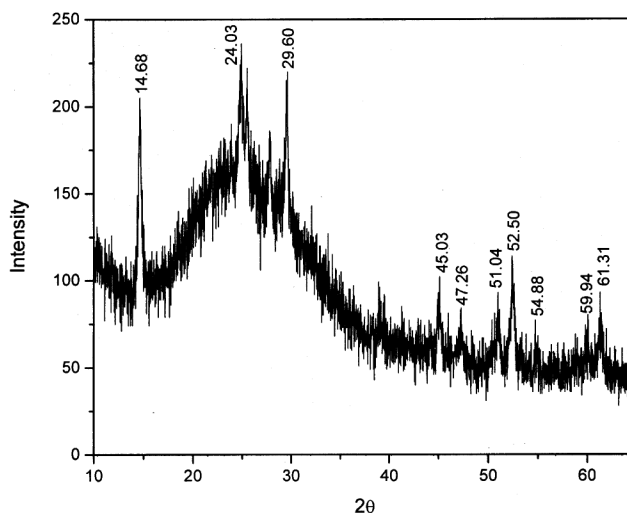


Figure 4. Powder diffraction pattern of precipitate in high-Al sample. The pattern matches with that of AlF_3 (JCPDS File No. 43-0435). Peak intensities are low due to very small amount of powder and background hump between 15 and 40°. 2θ is due to the glass slide.

Si. Increasing the pH or further dilution does not improve the quality of analyses. When present in higher quantity Al forms AlF_3 , as shown in Figure 4. The X-ray pattern was obtained from a PHILIPS X'Pert powder diffractometer with an accelerating voltage of 50 kV, a tube current of 40 mA and a scanning speed of 2 degrees 2θ per minute. Aluminum fluoride does not dissolve back into the solution and therefore, the deficiency of Al is still observed even after months of storage of the digested sample. Moreover, AlF_3 , as we observed, cannot be detected in solution. Its presence is known only when the

solution is poured from a volumetric flask after adjusting the dilution. Very tiny crystals stick to the wall of the flask. The dry powder is white in colour. In certain K-rich standard samples were observed substantially lower K in addition to lower Al. This loss is probably due to formation of cryolite (H_3AlF_6) and its alkalic analogues (Na_3AlF_6 and K_3AlF_6). When wet, cryolite is reportedly transparent as we observed in the case of AlF_3 . Most interestingly, such crystals sometimes formed and sometimes not even in the same sample when repeated. Probably their stability is sensitive to pH, availability of free F

ions and activity of Al. Presumably small differences in measurement of acid volumes show a significant effect.

Precipitation of other insoluble fluorides is known to occur during HF digestion of silicate rocks in bomb-digestion techniques³. We encountered only AlF_3 , seemingly because of the use of boric acid. Free F ions are neutralized by complexation with boric acid. While repeating digestion of a sample that persistently yielded AlF_3 precipitates, using 2 ml aqua regia, 4 ml HF and 70 ml 4% boric acid, we did accomplish a complete dissolution without any subsequent formation of precipitates.

Probably the 0.9 ml extra 4% boric acid per ml of HF used in this case prevented AlF_3 formation.

Although MW digestion is comparably easier and effective, like in any other digestion technique, the analyst needs to use his discretion. Any generalized recipe may not work for even a single group of samples, for example, the silicates. Individual sample chemistry needs to be judged and an appropriate strategy be designed. Although conventional B solution method may not give rise to kaolinite/pyrophyllite formation as Si is lost as SiF_4 , considerable Al is also evidently lost. Balaram⁴ emphasized this on evaporating away SiF_4 after MW treatment. His focus was on obtaining good analysis of rather difficult to dissolve refractory elements, but our purpose here is to ascertain quality analysis for common major elements. Considering the convenience of simultaneous Si analysis, the MW technique is preferable but with caution. AlF_3 and cryolite problems in high-Al samples need detailed study. Apart from the obvious loss of Al, the latter may also cause loss of Na and K. It is to be noted that early formation of AlF_3 or cryolite, in critical cases where HF

amount is just sufficient for the samples to be digested, may leave the acid + sample mixture deficient enough in F ions to prevent digestion to completion. Using 4 ml HF and a total of 70 ml boric acid instead of 3 ml HF and 50 ml boric acid yields better results. However, this should not be used as a general recipe and depending on the nature of the sample in hand different combinations may be tried, until complete digestion free of any precipitates is achieved. Apparently, boric acid prevents a host of other insoluble fluorides, which can accommodate various amounts of trace elements, to form and probably performs more than just making possible simultaneous Si measurements.

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