

MINERALOGICAL NOTES

Lithium borate decomposition of rocks, minerals, and ores

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Abstract

Lithium borate decomposition was tested for 26 National Bureau of Standard samples and 47 minerals. Those minerals that might occur in silicate rocks and that are only partly decomposed by this method include zircon, some metal oxides, some rare-earth phosphates, one rare-earth fluoride (fluocerite), and many sulfides. For some minerals, decomposition is facilitated by the addition of quartz to the sample.

Introduction

Of recently suggested single-solution techniques for the analysis of silicate rocks and minerals, one of the more versatile has been the lithium metaborate-dilute mineral acid method originally proposed by Ingamells (1964). The method has been adapted for use in emission spectrometry and flame photometry (Suhr and Ingamells, 1966; Engels and Ingamells, 1970), colorimetry (Ingamells, 1966; Shapiro, 1967), and atomic absorption spectrophotometry (Shapiro, 1967; Van Loon and Parissis, 1969; Medlin *et al.*, 1969; Abbey, 1970; Abbey *et al.*, 1974; Saavedra *et al.*, 1974). A 2:1 mixture of lithium tetraborate–lithium metaborate has also been used as a flux, followed by dissolution in dilute acid (Shapiro, 1975). The common minerals of silicate rocks—quartz, feldspars, amphiboles, pyroxenes, micas—are readily decomposed by lithium borate fusion; nitric, hydrochloric, or hydrofluoric acid treatment of the fusion yields solutions readily amenable to analytical techniques. The investigation reported here tested the method on accessory minerals that occur in silicate rocks and as inclusions in silicate minerals. The samples were selected from the study collections of the authors and the geologists at the Menlo Park Center of the U.S. Geological Survey and from the analyzed standards of the National Bureau of Standards (N.B.S.). The N.B.S. standards were examined by X-ray diffraction and polarizing microscopy to determine mineral composition.

Experimental

A 0.1000 g sample of minus 100 mesh was mixed with 0.7000 g of lithium metaborate. A second 0.1000

g portion was mixed with 0.7000 g of a 2:1 mixture of lithium tetraborate–lithium metaborate. The mixtures were transferred to pre-ignited high-purity graphite crucibles and ignited in a muffle furnace for 15 minutes at 950°C. The molten beads were poured into 250 ml polypropylene beakers containing 100 ml of 4 percent (by volume) nitric acid. The solutions were stirred magnetically for 10 minutes and then filtered through 9 cm hardened fast-filtering papers. The stirring bars were wiped with additional pieces of filter paper that were added to the filter funnels. The filter papers were washed 20 times with distilled water and placed in pre-ignited weighed porcelain crucibles. An additional porcelain crucible was used as a tare. The papers were ashed in an oxidizing atmosphere and the residues ignited for one hour at 600°C. The residues were weighed and examined by X-ray diffraction and polarizing microscopy.

Results and discussion

Fusion results for N.B.S. standards are listed in Table 1. Assorted mineral-fusion results are listed in Table 2. Considerable variations were found in the decomposition efficacy and in the pouring characteristics of the fusions. Fusions from many minerals could be poured completely from the graphite crucibles, and the residues after acid dissolution weighed less than 0.5 mg, that is, less than one-half percent of the sample weight. Fusions from other minerals could be poured completely, but significant amounts of unattacked material were found after the acid treatment. Fusions from some minerals stuck in part to the graphite crucibles and could not be poured completely; consequently, for these fusions the per-

TABLE I. Percent undecomposed and characteristics of residue from fusions of N.B.S. standards

N.B.S. no. and name	Principal components of N.B.S. standard	Residue (weight percent of N.B.S. sample)		Remarks
		F l u x		
		LiBO ₂	Mixed	
25c Manganese Ore	Pyrolusite, MnO ₂	< 0.5 *	< 0.5	Cloudy acid solution containing 2 Li ₂ B ₄ O ₇ ·1 LiBO ₂ fusion cleared with a few drops 30% H ₂ O ₂ . Pourable with 50 mg sample, 100 mg quartz, 700 mg LiBO ₂ plus H ₂ O ₂ . 0.7% residue.
27c Mesabi Iron Ore	Hematite, Fe ₂ O ₃	.5 *	.9 *	Pourable with 30 mg sample, 100 mg quartz, 700 mg LiBO ₂ . 1.0% residue.
27e Sibley Iron Ore	Hematite, Fe ₂ O ₃	.7 *	.5 *	Pourable with 30 mg sample, 100 mg quartz, 700 mg LiBO ₂ . 0.7% residue.
28a Norrie Iron Ore	Hematite, Fe ₂ O ₃	.6 *	.5 *	Pourable with 30 mg sample, 100 mg quartz, 700 mg LiBO ₂ . 1.0% residue.
56b Phosphate Rock	Fluorapatite, Ca ₅ (PO ₄) ₃ F	< .5	< .5	
69A Bauxite	Gibbsite, Al(OH) ₃	< .5	< .5	
71 Calcium Molybdate	Powellite, CaMoO ₄	< .5	---	
76 Burned Refractory	Sillimanite, Al ₂ SiO ₅	< .5	---	
79 Fluorspar	Cristobalite, SiO ₂	< .5	< .5	
89 Lead-Barium Glass	Fluorite, CaF ₂	< .5	---	
97 Flint Clay	Kaolinite, Al ₂ Si ₂ O ₅ (OH) ₄	< .5	---	
98 Plastic Clay	Kaolinite, Al ₂ Si ₂ O ₅ (OH) ₄ Quartz, SiO ₂	< .5	---	
102 Silica Brick	Muscovite, KAl ₂ (AlSi ₃) ₀ 10(OH) ₂	.6	---	
103a Chrome Refractory	Tridymite, SiO ₂	32.7	34.6	Residue reduced to 12% with 50 mg sample, 100 mg quartz, 1.05 g LiBO ₂ .
104 Burned Magnesite	Chromite, (Fe,Mg)(Cr,Al) ₂ O ₄	< .5	< .5	
113 Zinc Ore	Periclase, MgO	34.3	79.3	LiBO ₂ -quartz fusion residue not reduced.
120 Phosphate Rock	Zincite, ZnO	.6	< .5	
137 Tin Ore, Bolivia	Sphalerite, ZnS	29.3	70.1	Residue reduced to 2.2% with 50 mg sample, 100 mg quartz, 1.05 g LiBO ₂ .
138 Tin Ore, Netherlands East Indies	Fluorapatite, Ca ₅ (PO ₄) ₃ F	37.0 *	20.3 *	LiBO ₂ -quartz fusion not pourable.
154 Titanium Oxide	Cassiterite, SnO ₂	< .5	28.6 32.4	Cloudy acid solution containing LiBO ₂ fusion cleared with a few drops 30% H ₂ O ₂ . Acid treated 2 Li ₂ B ₄ O ₇ ·1 LiBO ₂ fusion did not clear with H ₂ O ₂ .
181 Lithium Ore	Rutile, TiO ₂	< .5	.5	
182 Lithium Ore	Spodumene, LiAlSi ₂ O ₆	< .5	.5	
183 Lithium Ore	Petalite, LiAlSi ₄ O ₁₀	< .5	< .5	
671 Nickel Oxide No. 1	Lepidolite, K(Li,Al) ₃ (Si,Al) ₄ O ₁₀ (F,OH) ₂	45.8 *	---	LiBO ₂ -quartz fusion not pourable.
672 Nickel Oxide No. 2	Bunsenite, NiO	*	---	Not filtered. Residue not determined. Pourable with 50 mg sample, 100 mg quartz, 700 mg LiBO ₂ . 0.6% residue.
673 Nickel Oxide No. 3	Bunsenite, NiO	*	---	Not filtered. Residue not determined. Pourable with 50 mg sample, 100 mg quartz, 700 mg LiBO ₂ . <0.5% residue.

* Part of hot fusion stuck to crucible and was not recovered; therefore reported residue is less than total residue.

† --- = Not fused with mixed flux.

cent residue shown in the tables is less than the total residue. Fusions from two minerals, chalcocite and turquoise, stuck completely, but the cooled fused beads could be pried from the crucibles so that the degree of decomposition could be determined. Fusions from some minerals that would not pour were rendered completely pourable by the addition of high-purity quartz. Other fusions could not be made pourable even with the addition of quartz.

The decomposition and pouring efficiency of the two fluxes differed little. Lithium metaborate decomposition was markedly superior for one mineral—rutile (N.B.S. 154); pouring qualities excelled for one mineral—galena. The 2 Li₂B₄O₇·1 LiBO₂ mixture provided better pouring qualities for pyrolusite, turquoise, and vonsenite.

A second small group of five N.B.S. samples was ignited with LiBO₂ and the 2 Li₂B₄O₇·1 LiBO₂ mixture as described above, but for a period of 45 minutes. Neither pouring qualities nor decomposition properties were improved: fusions of N.B.S. samples 27c, 138, and 671 neither poured nor dissolved completely. Fusion residues of N.B.S. samples 103a and 113 were of the same magnitude as those residues from the 15-minute fusions.

The residues contained varying amounts of graphite that could only be estimated by microscopic observation. The graphite content is probably related to the number of times the crucible has been used, for with continued use the cohesion of graphite particles decreases and graphite spalls from the inside walls of the crucible onto the fusion. The fusion time is too

TABLE 2. Percent undecomposed and characteristics of residue from mineral fusions

Mineral	General chemical formula	Residue (weight percent of mineral)		Remarks
		F l u x		
		LiBO ₂	Mixed	
Actinolite	Ca ₂ (Mg,Fe) ₅ [Si ₈ O ₂₂](OH,F) ₂	< 0.5	< 0.5	
Albite	NaAlSi ₃ O ₈	< .5	< .5	
Allanite	(Ce,Ca,Y) ₂ (Al,Fe) ₃ Si ₃ O ₁₂ (OH)	< .5	< .5	
Anhydrite	CaSO ₄	< .5	< .5	
Ankerite	Ca(Mg,Fe ⁺² ,Mn)(CO ₃) ₂	< .5	< .5	
Apatite, Montana	Ca ₅ (PO ₄) ₃ (OH,F,Cl)	< .5	< .5	
Apatite, Peru	Ca ₅ (PO ₄) ₃ (OH,F,Cl)	< .5	< .5	
Apatite, Quebec	Ca ₅ (PO ₄) ₃ (OH,F,Cl)	< .5	< .5	
Bastnaesite	(Ce,La)(CO ₃)F	20.4	20.3	
Beryl, Golden	Be ₃ Al ₂ [Si ₆ O ₁₈]	< .5	< .5	
Chalcocite	Cu ₂ S	91.7*	82.4*	Not pourable. Beads cooled; removed from crucibles; dissolved in 45 min.
Chalcopyrite	CuFeS ₂	55.2*	40.9*	
Chromite	FeCr ₂ O ₄	38.7	44.3	
Columbite	(Fe,Mn)(Cb,Ta) ₂ O ₆	46.4	46.9	
Corundum	αAl ₂ O ₃	< .5	.8	Cloudy acid solutions containing fusions cleared with a few drops 30% H ₂ O ₂ .
			< .5	
Eudialyte	Na ₄ (Ca,Fe,Ce,Mn) ₂ ZrSi ₆ O ₁₇ (OH,Cl) ₂	.5	.5	
Euxenite	(Y,Ca,Ce,U,Th)(Nb,Ta,Ti) ₂ O ₆	< .5	< .5	
Ferberite	FeWO ₄	< .5	.5	>100 < 50 mesh (Cloudy acid solutions >200 <100 mesh {containing fusions cleared {with a few drops 30% H ₂ O ₂ .
Fergusonite	Y(Nb,Ta) ₂ O ₄	.8	.6	
Fluocerite	(Ce,La,Y)F ₃	5.4	5.8	
Franklinite	ZnFe ₂ O ₄	< .5*	.6*	LiBO ₂ -quartz fusion not pourable.
Gadolinite	Be ₂ FeY ₂ O ₂ (SiO ₄) ₂	< .5	< .5	
Galena	PbS	34.6	13.2*	
Garnet, almandine (Alaska)	Fe ₃ Al ₂ (SiO ₄) ₃	< .5	< .5	
Garnet, almandine (Idaho)	Fe ₃ Al ₂ (SiO ₄) ₃	< .5	< .5	
Goethite	FeO(OH)	< .5*	< .5*	Pourable with 30 mg sample, 100 mg quartz, 700 mg LiBO ₂ . 1.0% residue.
Griphite	(Na,Ca,Mn,Fe) ₃ (Al,Mn) ₂ (PO ₄) _{2.5} (OH) ₂	< .5	< .5	
Ilmenite	FeTiO ₃	15.6*	.7*	
Magnetite	FeFe ₂ O ₄	< .5*	< .5*	LiBO ₂ -quartz fusion not pourable.
Monazite	(Ce,La,Th)PO ₄	11.8	27.4	
Olivine	(Mg,Fe) ₂ [SiO ₄]	< .5	< .5	
Pyrite	FeS ₂	39.7	25.6	
Pyrolusite	MnO ₂	< .5*	< .5	Cloudy acid solution containing 2 Li ₂ B ₄ O ₇ .1 LiBO ₂ fusion cleared with a few drops 30% H ₂ O ₂ .
Quartz	SiO ₂	< .5	< .5	
Scheelite	CaWO ₄	.5	< .5	
Sphene	CaTi[SiO ₄](O,OH,F)	< .5	< .5	
Spinel	MgAl ₂ O ₄	.5	---†	
Staurolite	(Fe,Mg) ₂ (Al,Fe) ₃ O ₆ [SiO ₄] ₄ (O,OH) ₂	< .5	< .5	
Tourmaline (elbaite)	Na(Li,Al) ₃ Al ₆ (BO ₃) ₃ (Si ₆ O ₁₈)(OH) ₄	< .5	< .5	
Tourmaline (indicolite)	Na(Li,Al) ₃ Al ₆ (BO ₃) ₃ (Si ₆ O ₁₈)(OH) ₄	< .5	< .5	
Turquoise	CuAl ₆ (PO ₄) ₄ (OH) ₈ ·5H ₂ O	< .5*	< .5	LiBO ₂ fusion not pourable. Bead cooled; removed from crucible; dissolved in 45 min.
Vesuvianite	Ca ₁₀ Mg ₂ Al ₄ (SiO ₄) ₅ (Si ₂ O ₇) ₂ (OH) ₄	< .5	< .5	
Vivianite	Fe ₃ (PO ₄) ₂ ·8H ₂ O	< .5	< .5	
Vonsenite	(Fe ²⁺ ,Mg) ₂ Fe ³⁺ BO ₅	< .5*	< .5	
Wolframite	(Fe,Mn)WO ₄	1.4	2.6	
Xenotime	YPO ₄	4.1	3.9	
Zircon	ZrSiO ₄	21.4	20.3	

* All or part of hot fusion stuck to crucible. For fusions in which part stuck to the crucible, reported residues are less than total residues.

† --- = Not fused with mixed flux.

short to oxidize the graphite within the crucible. Thus the HNO₃ solutions always contain some suspended graphite. During the ashing of the filter paper, temperatures higher than 600°C were avoided so as not to alter the composition of the residue. At that temperature, the graphite did not oxidize.

Microscopic observation of residues obtained after filtering and ashing showed that in addition to remnants of the original sample, all of them contained anisotropic particles as well as diatom fragments, though they were present in amounts less than 0.1 mg. The particles ranged in size from 3 to 100 microns. Optical properties and X-ray diffraction analysis showed that the particles were mostly quartz and minor amounts of feldspar and mica. Microscopic and X-ray diffraction analysis of unused ashed filter paper revealed the presence of similar particles and diatom fragments.

Conclusions

The lithium borate–mineral acid method for the decomposition and dissolution of silicate rocks and minerals for quantitative chemical analysis is unsatisfactory in attacking some accessory minerals. Rocks and minerals containing oxides of the transition elements, rare-earth phosphates and fluorides, sulfides, and zircon may not be decomposed completely or the melt may adhere to the crucible. The addition of quartz aids in the break-up of some minerals and in the pouring of some fusions.

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