

**BARAHONAITE-(Al) AND BARAHONAITE-(Fe),  
 NEW Ca–Cu ARSENATE MINERAL SPECIES, FROM MURCIA PROVINCE,  
 SOUTHEASTERN SPAIN, AND GOLD HILL, UTAH**

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ABSTRACT

The new mineral species barahonaite-(Fe) and barahonaite-(Al), simplified as  $(\text{Ca,Cu,Na,Fe}^{3+},\text{Al})_{12}\text{Fe}^{3+}_2(\text{AsO}_4)_8(\text{OH})_n \cdot n\text{H}_2\text{O}$  and  $(\text{Ca,Cu,Na,Al})_{12}\text{Al}_2(\text{AsO}_4)_8(\text{OH})_n \cdot n\text{H}_2\text{O}$ , respectively, occur at the Dolores prospect in Murcia Province, southeastern Spain. Barahonaite-(Al) also occurs at the former Gold Hill mine in Tooele County, Utah. The minerals form beads, coalesced beads, and crusts of submillimetric thickness whose surfaces commonly glisten because of the presence of plates, up to 50  $\mu\text{m}$  in diameter (Utah), and razor-thin, tabular, composite crystals, up to 20  $\mu\text{m}$  long (Spain). Barahonaite-(Al) is pale blue, brittle, transparent to translucent, soft, nonfluorescent, and has a white streak and  $D_{\text{meas}}$  3.03  $\text{g}/\text{cm}^3$ ; barahonaite-(Fe) is similar, but is yellow with a greenish tint and has a white to pale yellow streak. Both minerals are readily soluble in 10% HCl. Barahonaite-(Fe) is biaxial negative,  $\alpha$  1.664(2),  $\beta \approx \gamma$ ,  $\gamma$  1.677(2),  $2V_{\text{meas}}$  45–80°; the indices of refraction of barahonaite-(Al) are  $\alpha$  1.616(2),  $\gamma$  1.622(2). The compositions for barahonaite-(Fe) and barahonaite-(Al) from Spain, as determined with an electron microprobe, are, respectively, Na<sub>2</sub>O 2.07, 1.65, MgO 0.14, 0.00, CaO 12.96, 15.71, CuO 12.41, 14.59, Al<sub>2</sub>O<sub>3</sub> 1.71, 9.52, Fe<sub>2</sub>O<sub>3</sub> 13.78, 0.10, SiO<sub>2</sub> 0.33, 0.14, P<sub>2</sub>O<sub>5</sub> 0.42, 0.35, As<sub>2</sub>O<sub>5</sub> 41.18, 42.16, SO<sub>3</sub> 0.29, 1.24, Cl 0.91, 0.06, H<sub>2</sub>O (by difference) 14.01, 14.49, which correspond to  $(\text{Ca}_{4.95}\text{Cu}_{3.34}\text{Na}_{1.43}\text{Mg}_{0.07}\text{Fe}^{3+}_{1.70}\text{Al}_{0.72})_{\Sigma 12.21}\text{Fe}^{3+}_{2.00}[(\text{As}_{0.96}\text{P}_{0.02}\text{S}_{0.01}\text{Si}_{0.01})\text{O}_4]_8[(\text{OH})_{6.82}\text{Cl}_{0.55}]_{\Sigma 7.37} \cdot 13.2\text{H}_2\text{O}$  and to  $(\text{Ca}_{5.75}\text{Cu}_{3.77}\text{Na}_{1.09}\text{Al}_{1.84}\text{Fe}^{3+}_{0.03})_{\Sigma 12.48}\text{Al}_{2.00}[(\text{As}_{0.94}\text{S}_{0.04}\text{P}_{0.01}\text{Si}_{0.01})\text{O}_4]_8[(\text{OH})_{7.95}\text{Cl}_{0.04}]_{\Sigma 7.99} \cdot 12.5\text{H}_2\text{O}$  for  $X\text{O}_4 = 8$ . Indexing of the powder-diffraction patterns gave  $a$  10.161(7),  $b$  22.39(2),  $c$  10.545(10) Å,  $\beta$  93.3(1)° for barahonaite-(Fe), and  $a$  9.964(3),  $b$  22.43(1),  $c$  10.555(6) Å,  $\beta$  92.76(6)° for barahonaite-(Al). The strongest lines in the powder pattern [ $d$  in Å( $J$ )( $hkl$ )] are 22.0(100)(010), 11.2(70)(020), 5.068(20)(200), 3.345(20)(023, 310), 2.763(30)(053), 2.659(20)( $\bar{1}72$ ), and 2.541(20)(400) for barahonaite-(Fe), and 22.0(100)(010), 11.16(70)(020), 4.983(50)(200), and 3.333(45)(250, $\bar{1}13$ ) for barahonaite-(Al). The compositions and X-ray data suggest a possible overall relationship to the smolianovite group, and a close relationship between attikaite and barahonaite-(Al). The new name barahonaite-(Fe) honors Antonio Barahona (b. 1937) of Madrid, Spain, who collected the original specimens, and barahonaite-(Al) is the Al-dominant analog of barahonaite-(Fe).

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**Keywords:** barahonaite-(Fe), barahonaite-(Al), new mineral species, arsenates, electron-microprobe compositions, X-ray powder data, smolianinovite group, attikaite, Dolores prospect, Spain, Gold Hill mine, Utah.

## SOMMAIRE

Les nouvelles espèces minérales barahonaite-(Fe) et barahonaite-(Al), dont les formules simplifiées sont  $(\text{Ca,Cu,Na,Fe}^{3+}, \text{Al})_{12}\text{Fe}^{3+}_2(\text{AsO}_4)_8(\text{OH})_x \cdot n\text{H}_2\text{O}$  et  $(\text{Ca,Cu,Na,Al})_{12}\text{Al}_2(\text{AsO}_4)_8(\text{OH})_x \cdot n\text{H}_2\text{O}$ , respectivement, ont été découvertes à l'indice Dolores, province de Murcia, dans le sud-est de l'Espagne. Le barahonaite-(Al) est aussi présente à l'ancienne mine Gold Hill, comté de Tooele, au Utah. Ces minéraux se présentent en perles, en perles coalescées, et en encroûtements submillimétriques dont la surface brille à cause de la présence de plaquettes atteignant 50  $\mu\text{m}$  de diamètre (Utah), et de cristaux composés tabulaires très minces, jusqu'à 20  $\mu\text{m}$  en longueur (Espagne). Le barahonaite-(Al) est bleu pâle, cassante, transparente à translucide, tendre, non fluorescente, avec une rayure blanche et une densité mesurée de 3.03  $\text{g/cm}^3$ ; le barahonaite-(Fe) est semblable, mais plutôt jaune verdâtre, avec une rayure blanche à jaune pâle. Les deux minéraux sont facilement solubles dans l'acide HCl (10%). Le barahonaite-(Fe) est biaxe négative,  $\alpha$  1.664(2),  $\beta \approx \gamma$ ,  $\gamma$  1.677(2),  $2V_{\text{mes}}$  45–80°; les indices de réfraction de la barahonaite-(Al) sont  $\alpha$  1.616(2),  $\gamma$  1.622(2). Les compositions de la barahonaite-(Fe) et la barahonaite-(Al) de l'Espagne (données obtenues avec une microsonde électronique) sont, respectivement,  $\text{Na}_2\text{O}$  2.07, 1.65,  $\text{MgO}$  0.14, 0.00,  $\text{CaO}$  12.96, 15.71,  $\text{CuO}$  12.41, 14.59,  $\text{Al}_2\text{O}_3$  1.71, 9.52,  $\text{Fe}_2\text{O}_3$  13.78, 0.10,  $\text{SiO}_2$  0.33, 0.14,  $\text{P}_2\text{O}_5$  0.42, 0.35,  $\text{As}_2\text{O}_5$  41.18, 42.16,  $\text{SO}_3$  0.29, 1.24,  $\text{Cl}$  0.91, 0.06,  $\text{H}_2\text{O}$  (par différence) 14.01, 14.49, ce qui correspond à  $(\text{Ca}_{4.95}\text{Cu}_{3.34}\text{Na}_{1.43}\text{Mg}_{0.07}\text{Fe}^{3+}_{1.70}\text{Al}_{0.72})_{\Sigma 12.21}\text{Fe}^{3+}_{2.00}[(\text{As}_{0.96}\text{P}_{0.02}\text{S}_{0.01}\text{Si}_{0.01})\text{O}_4]_8[(\text{OH})_{6.82}\text{Cl}_{0.55}]_{\Sigma 7.37} \cdot 13.2\text{H}_2\text{O}$  et à  $(\text{Ca}_{5.75}\text{Cu}_{3.77}\text{Na}_{1.09}\text{Al}_{1.84}\text{Fe}^{3+}_{0.03})_{\Sigma 12.48}\text{Al}_{2.00}[(\text{As}_{0.94}\text{S}_{0.04}\text{P}_{0.01}\text{Si}_{0.01})\text{O}_4]_8[(\text{OH})_{7.95}\text{Cl}_{0.04}]_{\Sigma 7.99} \cdot 12.5\text{H}_2\text{O}$  pour  $\text{XO}_4 = 8$ . L'indexation des spectres de diffraction, méthode des poudres, a donné les paramètres  $a$  10.161(7),  $b$  22.39(2),  $c$  10.545(10) Å,  $\beta$  93.3(1)° pour la barahonaite-(Fe), et  $a$  9.964(3),  $b$  22.43(1),  $c$  10.555(6) Å,  $\beta$  92.76(6)° pour la barahonaite-(Al). Les raies les plus intenses du spectre de diffraction obtenu sur poudre [ $d$  en Å( $f$ )( $hkl$ )] sont 22.0(100)(010), 11.2(70)(020), 5.068(20)(200), 3.345(20)(023, 310), 2.763(30)(053), 2.659(20)(172), et 2.541(20)(400) pour la barahonaite-(Fe), et 22.0(100)(010), 11.16(70)(020), 4.983(50)(200), et 3.333(45)(250,113) pour la barahonaite-(Al). Les compositions et les données de diffraction X font penser qu'il pourrait y avoir une relation avec le groupe de la smolianinovite, et une ressemblance entre l'attikaite et la barahonaite-(Al). Le nom barahonaite-(Fe) honore Antonio Barahona (né en 1937), de Madrid, Espagne, qui a découvert les échantillons originels; la barahonaite-(Al) est l'analogue à dominance d'aluminium de la barahonaite-(Fe).

(Traduit par la Rédaction)

**Mots-clés:** barahonaite-(Fe), barahonaite-(Al), nouvelles espèces minérales, arsenates, données de microsonde électronique, diffraction X sur poudre, groupe de la smolianinovite, attikaite, indice Dolores, Espagne, mine Gold Hill, Utah.

## INTRODUCTION

The Dolores prospect near the village of Pastrana, in the Province of Murcia of southeastern Spain, consists of a small lens, about  $0.2 \times 2 \times 10$  m, in which the primary sulfides have been completely oxidized to a supergene assemblage of more than 25 minerals, several of which are arsenates (Sainz de Baranda *et al.* 2003). The prospect is the type locality for cobalt-arthurite  $[\text{Co}^{2+}\text{Fe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$  (Jambor *et al.* 2002), and is designated the type locality for the new arsenate minerals barahonaite-(Fe) and barahonaite-(Al), described herein. The simplified compositions of barahonaite-(Fe) is  $(\text{Ca,Cu,Na,Fe}^{3+}, \text{Al})_{12}\text{Fe}^{3+}_2(\text{AsO}_4)_8(\text{OH})_x \cdot n\text{H}_2\text{O}$ , and that of barahonaite-(Al) is  $(\text{Ca,Cu,Na,Al})_{12}\text{Al}_2(\text{AsO}_4)_8(\text{OH})_x \cdot n\text{H}_2\text{O}$ , where  $n$  is probably 16–18 and  $x$  varies with the substitutions among the monovalent to trivalent cations in the main cation position within the simplified formula. Barahonaite-(Al) also occurs at the Gold Hill mine in Tooele County, western Utah (Kokinos & Wise 1993).

Barahonaite-(Fe) is named after Antonio Barahona (b. 1937) of Madrid, Spain, a well-known mineral collector who recognized the Dolores collecting site and provided the original specimens from it. Barahonaite-(Al) is the Al-dominant analog of barahonaite-(Fe). Its

name recognizes the mineralogical and compositional relationship with barahonaite-(Fe). The new minerals and mineral names have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA nos. 2006–51, 2006–52). Cotype specimens of barahonaite-(Fe) and barahonaite-(Al) are in the Canadian Museum of Nature at Ottawa, Ontario, under catalogue numbers CMNMC 85716 and CMNMC 85719, respectively.

## OCCURRENCE

A close-up photograph of the Dolores prospect and superb color illustrations of many of its secondary minerals, including arsenocrandallite, arsenogoyazite, conichalcite, cobaltarthurite, chlorargyrite, olivenite, azurite, cornwallite, pharmacosiderite, zálesíite, and lavendulan, have been published by Sainz de Baranda *et al.* (2003), who refer to barahonaite-(Fe) and barahonaite-(Al) as Unknown #1. The oxidation minerals occur as coatings and within closely spaced fractures in weathered siliceous and micaceous host-rocks. Pharmacosiderite and jarosite are the most intimately associated with barahonaite-(Fe) and barahonaite-(Al), and it is difficult to obtain pharmacosiderite-free X-ray patterns

even from the small amount of material required for Debye–Scherrer X-ray mounts.

Whereas both barahonaite-(Fe) and barahonaite-(Al) occur at the Dolores prospect, only the latter is present at Gold Hill. The Gold Hill mine, which has been inactive for more than 50 years, produced modest tonnages of polymetallic ores (Pb–Cu–Ag–Au, including As derived from arsenopyrite) in skarn and post-skarn replacement veins and bodies (Kokinos & Wise 1993). Oxidation in the mine extended to its deepest level, about 100 m below surface. Nearly all of the primary sulfides near the surface have been altered to arsenate and sulfate assemblages; one of the arsenate suites described by Kokinos & Wise (1993) was reported to contain an “unnamed Ca-arsenate”, and this mineral has since been determined to be barahonaite-(Al).

#### PHYSICAL PROPERTIES AND ASSOCIATIONS

Barahonaite-(Fe) occurs sparingly as isolated, rosette-like beads, up to about 200  $\mu\text{m}$  in diameter. The mineral forms sparse coatings on fracture surfaces, generally on a substrate of pharmacosiderite, and coalescences of glittering beads are the norm rather than the exception. Barahonaite-(Al) from Spain is similar, but much sparser, and only locally are the beads coalesced into aggregates of a few beads. Examination by scanning electron microscopy (SEM) indicates that the surface of the beads of barahonaite-(Fe) and barahonaite-(Al) consists of razor-thin, tabular, composite crystals whose maximum length is about 20  $\mu\text{m}$ . The crystal units are somewhat divergent, and the texture varies from rosette to boxwork-like (Figs. 1, 2). Barahonaite-(Al) from Utah, although rare, is more abundant than at the Spanish occurrence. The Utah material forms thin, smooth crusts of submillimetric thickness on weathered surfaces of fractures. The crusts are gradational to areas at which the surface of the coatings is hemispherical and glistens because of the presence of microscopic platy crystals. The plates are commonly curved, and their maximum size is  $\sim 50$   $\mu\text{m}$  in diameter and  $< 1$   $\mu\text{m}$  in thickness (Fig. 1d). Commonly associated with the Utah material is a clear to faintly bluish, glassy, almost amorphous Al silicate upon which crusts of barahonaite-(Al) have been deposited (Fig. 2a). The substrate silicate has Al:Si = 1:1 and contains about 6 wt.%  $\text{As}_2\text{O}_5$ . Arsenocrandallite and what is referred to here as “hyper-hydrated barahonaite-(Al)” are locally associated with the crusts. Although the crystallography of the hyper-hydrated phase (Fig. 2a) is not known, the phase differs notably from barahonaite-(Al) in giving much lower totals for microprobe-derived compositions.

The macroscopically distinct difference between barahonaite-(Fe) and barahonaite-(Al) is that the latter is pale blue and has a white streak, whereas barahonaite-(Fe), owing to its much higher Fe content, is greenish yellow and has a white to pale yellow streak. Both

minerals have a vitreous luster and are brittle, transparent to translucent, non-fluorescent, and are readily soluble without effervescence in 10% HCl at room temperature. Their hardnesses are not determinable, but may be 2–3; crusts are easily scratched with a fingernail, but this is likely the result of disaggregation of microscopic crystals rather than a true hardness. A density of 3.03  $\text{g}/\text{cm}^3$  was obtained for the Utah barahonaite-(Al) by suspension in heavy liquids. The calculated density varies from 2.89 to 3.06  $\text{g}/\text{cm}^3$ , depending on which value for  $\text{H}_2\text{O}$  is used; for the Utah material and the  $\text{H}_2\text{O}$  value obtained by thermogravimetric analysis,  $D_{\text{calc}}$  is 2.99  $\text{g}/\text{cm}^3$  with  $Z = 2$ .

Grains of barahonaite-(Fe) examined in immersion oil are 5–10  $\mu\text{m}$  in maximum dimension and, at 590 nm, have  $\alpha$  1.664(2),  $\beta \approx \gamma$ ,  $\gamma$  1.677(2). The mineral is biaxial (–), with  $2V$  in the range 45–80° by direct measurement and the Kamb method;  $X$  is perpendicular to the plate, and  $Y$  and  $Z$  are within the plate. No dispersion or pleochroism was observed. Single-crystal portions of barahonaite-(Al) are only  $\sim 1$   $\mu\text{m}$ , with no possibility of determining the optic sign, pleochroism, or dispersion. Under crossed polarizers, the interference color is grey to yellow, and the measured indices of refraction are  $\alpha$  1.616(2) and  $\gamma$  1.622(2). The mineral is presumed to be biaxial (–), analogous to the optic sign for barahonaite-(Fe).

#### CHEMICAL COMPOSITION

Electron-microprobe compositions of barahonaite-(Fe) and barahonaite-(Al) were obtained in the wavelength-dispersion mode at 15 kV and 5 nA with beam diameters of 5  $\mu\text{m}$  and 10  $\mu\text{m}$ , and with the following standards: albite (Na), diopside (Mg, Ca, Si), kyanite (Al), fayalite (Fe), apatite (P), arsenopyrite (As), and scapolite (Cl). The results are summarized in Table 1, wherein the empirical formulas are expressed on the basis of  $\text{XO}_4 = 8$ , and  $(\text{Fe}^{3+} + \text{Al})$  in excess of 2.00 *apfu* (atoms per formula unit) has been combined with the divalent cations. The simplified formula for barahonaite-(Fe) is  $(\text{Ca,Cu,Na,Fe}^{3+},\text{Al})_{12}\text{Fe}^{3+}_2(\text{AsO}_4)_8(\text{OH,Cl})_x \cdot n\text{H}_2\text{O}$ , and that for barahonaite-(Al) is  $(\text{Ca,Cu,Na,Al})_{12}\text{Al}_2(\text{AsO}_4)_8(\text{OH,Cl})_x \cdot n\text{H}_2\text{O}$ , where  $n$  is probably 16–18 and  $x$  varies with the substitutions among the monovalent to trivalent cations at the Ca-dominant formula position. Numerous microprobe-derived compositions in addition to those in Table 1 indicate that the Fe–Al solid-solution series is complete (Fig. 3). If the first part of the formula of either of the minerals is taken as  $\text{A}^{2+}_{12}\text{B}^{3+}_2(\text{AsO}_4)_8$ , with only divalent cations in the A formula position and only As in  $\text{XO}_4$ , then only 6 (OH) are required to maintain charge balance, and the remaining two positions could be occupied by  $\text{H}_2\text{O}$ . However, all analyses indicate an excess (*i.e.*,  $> 2$  *apfu*) of trivalent ions, and the excess has been allocated to the A position. The surplus of  $(\text{Fe}^{3+}, \text{Al})$  for the compositions in Table 1 varies from 1.87 to 2.54

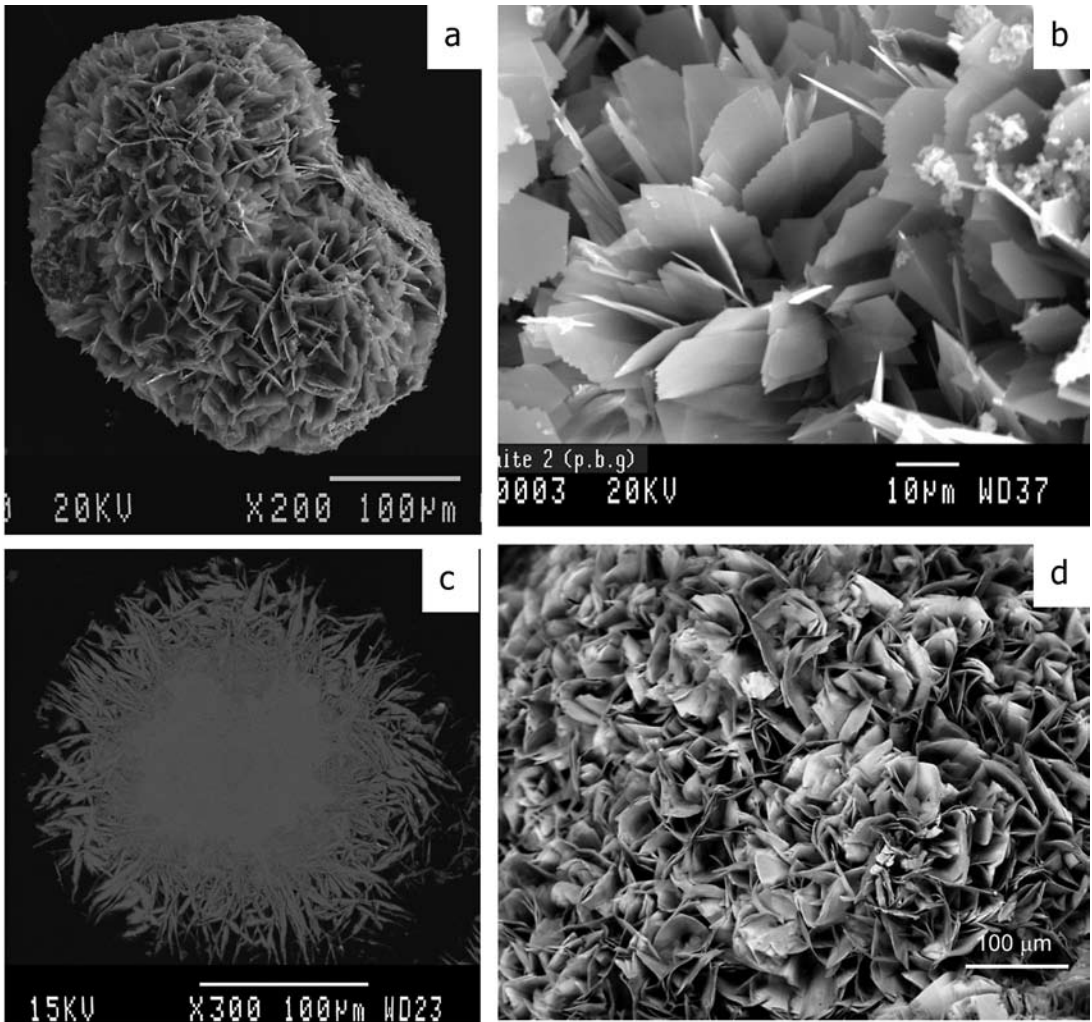


FIG. 1. SEM images of barahonaite-(Al) from Spain, showing (a) the boxwork-like form of the surface of one of the beads, (b) the bladed habit of the crystal aggregates, and (c) the polished surface of the bead for which the composition is given in Table 1. (d) Barahonaite-(Al) from Gold Hill, Utah, showing the curved-plate morphology of the crystals.

*apfu*, and with the transfer of this amount, the sum at *A* approximates 12 *apfu*. The assignment of 2 atoms of Fe in barahonaite-(Fe), and of 2 Al in barahonaite-(Al), to a specific and stoichiometric position (*B*) is in accord with the formula of fahleite, which is a member of the smolianinovite group and which is generally given as  $\text{CaZn}_5\text{Fe}^{3+}_2(\text{AsO}_4)_6 \cdot 14\text{H}_2\text{O}$ . The relationship of the barahonaite minerals to the smolianinovite group is discussed in a later section. It is recognized that for the barahonaite minerals, the grouping of monovalent, divalent, and trivalent ions into the *A* formula position is a gross simplification because *A* probably encompasses

a multitude of crystallographic sites; however, in light of the non-stoichiometry involving both individual cations and their combinations, a generalization is considered to be warranted until crystal-structure data are available.

Also listed in Table 1 is the microprobe-derived composition of attikaite, which was recently described as a new mineral by Chukanov *et al.* (2007). As is evident in Table 1, attikaite and barahonaite-(Al) have strong similarities in composition; however, as is discussed farther below, the differences between the two minerals suggest that they are not identical.

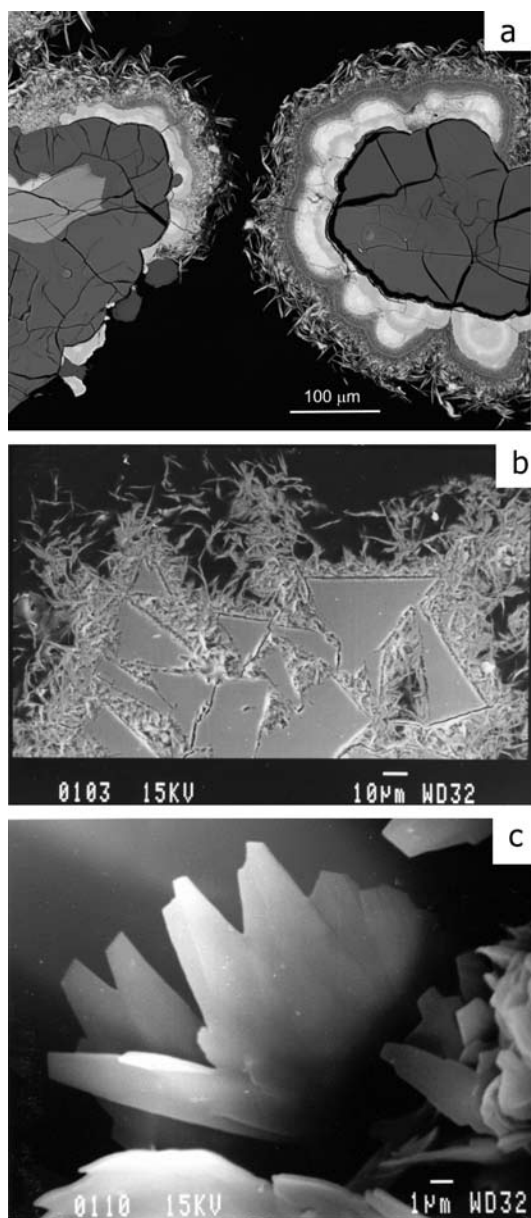


FIG. 2. (a) SEM image of a polished surface of barahonaite-(Al) from Gold Hill, Utah. The cracked, homogeneous core on the right is the amorphous As-bearing Al silicate, which is rimmed by barahonaite-(Al) (white). The dark zone between the [white] barahonaite-(Al) and the peripheral cross-sectioned plates is compositionally similar to barahonaite-(Al) but is hyper-hydrated. The aggregate on the left has a smaller amount of the hyper-hydrated phase. (b) A polished surface showing barahonaite-(Fe) as a coating on coarse-grained pharmacosiderite. (c) Tapered aggregates of bladed barahonaite-(Fe).

### Thermogravimetric (TG) and differential thermal (DT) analyses

The H<sub>2</sub>O content of barahonaite-(Al) was obtained from hand-picked material from the Utah locality, which is the only site that has enough material to obtain an adequate amount of concentrate. The total weight of concentrate obtained was about 4 mg, and this was split into roughly equal portions, with one held in reserve. The TG-DT sample, weighing 2.04 mg, was used first to obtain an X-ray diffractogram, from which we concluded that the amount of impurity, in part arsenocrandallite, was likely <5% by weight. Prior to obtaining simultaneous DT-TG analyses, the apparatus was tested by using 1 mg of scorodite [FeAsO<sub>4</sub>•2H<sub>2</sub>O] and a heating rate of 10°C/min. The test showed a loss of 1.2 wt.% to 155°C, attributable to adsorbed H<sub>2</sub>O, and a rapid loss of 16.4 wt.% (theoretical H<sub>2</sub>O 15.6%) from 155 to 255°C. A further gradual and continuous loss of 5.6 wt.% occurred from 255 to 920°C.

The subsequent test of barahonaite-(Al) at the same rate of heating showed that loss of H<sub>2</sub>O begins immediately upon heating (Fig. 4); the loss amounts to 4.7 wt.% to 189°C, and is accompanied by weak endothermic reactions. That this early-released water is at least partly structural rather than absorbed is also indicated by a change in the X-ray pattern after the mineral has been analyzed by electron microprobe. Beyond 189°C, the TG curve begins to level off and the main structural H<sub>2</sub>O-OH, totaling 13.3 wt.%, is evolved to 800°C; within this temperature span, the loss of 7.60 wt.% is

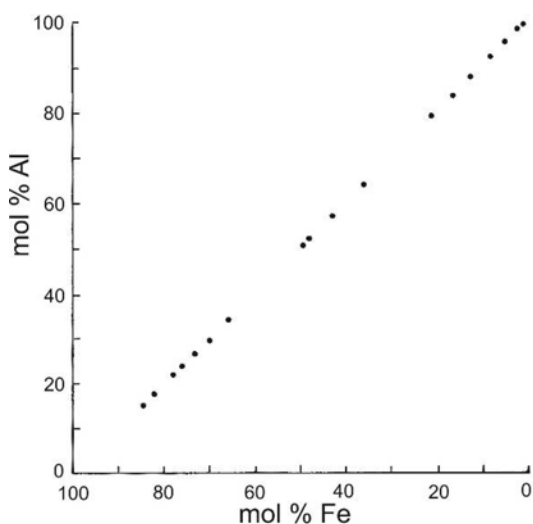


FIG. 3. Mol. % Fe versus mol. % Al for various microprobe-derived compositions of barahonaite-(Al) and barahonaite-(Fe).

TABLE 1. COMPOSITION OF BARAHONAITE-(Fe), BARAHONAITE-(Al) AND ATTIKAITE

	Barahonaite-(Fe)				Barahonaite-(Al)			Attikaite	
	Spain <sup>a</sup>		Spain <sup>b</sup>		Utah <sup>c</sup>		Utah <sup>d</sup>	Utah <sup>e</sup>	Greece <sup>f</sup>
Na <sub>2</sub> O	2.07	1.39-2.73	1.65	1.13-1.88	0.44	0.41-0.48	0.42	1.93	
MgO	0.14	0.07-0.56	0.00		0.01	0.00-0.06	0.01	0.08	0.17
CaO	12.96	12.10-13.64	15.71	14.98-16.12	13.63	13.34-13.95	13.05	14.35	17.48
CuO	12.41	12.01-12.91	14.59	13.95-15.12	15.27	14.83-15.77	14.62	13.33	16.28
Al <sub>2</sub> O <sub>3</sub>	1.71	1.39-2.13	9.52	9.30-9.78	11.13	10.87-11.48	10.66	9.20	10.61
Fe <sub>2</sub> O <sub>3</sub>	13.78	13.18-14.68	0.10	0.00-0.26	0.40	0.26-0.62	0.38	0.16	0.12
SiO <sub>2</sub>	0.33	0.18-0.44	0.14	0.10-0.18	0.42	0.35-0.51	0.40	0.70	
P <sub>2</sub> O <sub>5</sub>	0.42	0.05-1.18	0.35	0.06-0.55	0.18	0.00-0.43	0.17		0.89
As <sub>2</sub> O <sub>5</sub>	41.18	39.95-42.66	42.16	41.18-42.84	44.07	43.28-44.96	42.21	40.93	45.45
SO <sub>3</sub>	0.29	0.08-0.54	1.24	1.02-1.33	0.07	0.00-0.22	0.07	0.06	1.39
Cl	0.91	0.66-1.25	0.06	0.02-0.13	0.14	0.05-0.25	0.13	1.30	
O=Cl	0.21		0.01		0.03		0.03	0.29	
[H <sub>2</sub> O]	14.01		14.49		14.27		17.9	18.25	7.61
Total	100		100		100		99.99	100	100

Total Fe as Fe<sub>2</sub>O<sub>3</sub>; H<sub>2</sub>O by difference except as noted below. Formulas are calculated for XO<sub>4</sub> = 8, except for attikaite. Electron-microprobe data, expressed in weight %, with ranges given.

<sup>a</sup> barahonaite-(Fe), Spain, average result of seven analyses:

(Ca<sub>4.95</sub>Cu<sub>3.34</sub>Na<sub>1.43</sub>Mg<sub>0.07</sub>Fe<sub>1.70</sub>Al<sub>0.72</sub>Si<sub>1.21</sub>Fe<sub>2.00</sub>[(As<sub>0.96</sub>P<sub>0.02</sub>S<sub>0.01</sub>Si<sub>0.01</sub>)O<sub>4</sub>]<sub>8</sub>(OH)<sub>6.82</sub>Cl<sub>0.55</sub>]<sub>27.37</sub>•13.2H<sub>2</sub>O

<sup>b</sup> barahonaite-(Al), Spain, average result of six analyses:

(Ca<sub>2.75</sub>Cu<sub>3.77</sub>Na<sub>1.09</sub>Al<sub>1.84</sub>Fe<sub>3.1</sub>Si<sub>1.21</sub>Al<sub>2.00</sub>[(As<sub>0.94</sub>S<sub>0.04</sub>P<sub>0.01</sub>Si<sub>0.01</sub>)O<sub>4</sub>]<sub>8</sub>[(OH)<sub>7.95</sub>Cl<sub>0.41</sub>]<sub>27.09</sub>•12.5H<sub>2</sub>O

<sup>c</sup> barahonaite-(Al), Utah, average result of seven analyses (compact; H<sub>2</sub>O by difference):

(Ca<sub>4.94</sub>Cu<sub>3.56</sub>Na<sub>0.29</sub>Mg<sub>0.07</sub>Al<sub>1.24</sub>Fe<sub>3.1</sub>Si<sub>1.11</sub>Al<sub>2.00</sub>[(As<sub>0.97</sub>Si<sub>0.02</sub>P<sub>0.01</sub>)O<sub>4</sub>]<sub>8</sub>[(OH)<sub>7.37</sub>Cl<sub>0.08</sub>]<sub>27.45</sub>•12.4H<sub>2</sub>O

<sup>d</sup> barahonaite-(Al), Utah (compact, but with H<sub>2</sub>O by TG to 800°C):

(Ca<sub>2.94</sub>Cu<sub>3.99</sub>Na<sub>0.29</sub>Mg<sub>0.07</sub>Al<sub>1.44</sub>Fe<sub>3.1</sub>Si<sub>1.11</sub>Al<sub>2.00</sub>[(As<sub>0.97</sub>Si<sub>0.02</sub>P<sub>0.01</sub>)O<sub>4</sub>]<sub>8</sub>[(OH)<sub>7.37</sub>Cl<sub>0.08</sub>]<sub>27.45</sub>•17.4H<sub>2</sub>O

<sup>e</sup> barahonaite-(Al), Utah (plate cross-section), result of single analysis:

(Ca<sub>5.55</sub>Cu<sub>3.64</sub>Na<sub>1.35</sub>Mg<sub>0.04</sub>Al<sub>1.92</sub>Fe<sub>3.1</sub>Si<sub>1.22</sub>Al<sub>2.00</sub>[(As<sub>0.97</sub>Si<sub>0.03</sub>)O<sub>4</sub>]<sub>8</sub>[(OH)<sub>6.67</sub>Cl<sub>0.80</sub>]<sub>27.47</sub>•18.6H<sub>2</sub>O

<sup>f</sup> attikaite, average result of four analyses, with Fe as FeO rather than Fe<sub>2</sub>O<sub>3</sub> (Chukanov *et al.* 2007):

Ca<sub>2.94</sub>Cu<sub>1.93</sub>Al<sub>1.97</sub>Mg<sub>0.04</sub>Fe<sub>0.02</sub>[(As<sub>3.74</sub>S<sub>0.16</sub>P<sub>0.12</sub>)<sub>64.02</sub>O<sub>16.03</sub>](OH)<sub>8.87</sub>•2.05H<sub>2</sub>O, simplified as

Ca<sub>3</sub>Cu<sub>2</sub>Al<sub>2</sub>(AsO<sub>4</sub>)<sub>4</sub>(OH)<sub>4</sub>•2H<sub>2</sub>O.

accompanied by weak endotherms, and the remaining evolution (5.67 wt.%) is marked by a strong endotherm at 550°C. An additional loss of 1.2 wt.% occurs between 800 and 1000°C. Thus, the total loss to 800°C is 17.9 wt.%, and this value has been used in one of the formula calculations in Table 1. A SEM energy-dispersion analysis of the final TG product indicated that all of the Cl had also been evolved; however, this release would have little effect on the H<sub>2</sub>O–OH approximation because the amount of Cl substitution is low (Table 1).

### Infrared and Raman spectroscopy

Infrared spectra for barahonaite-(Fe) and barahonaite-(Al) from the Dolores prospect were obtained with a Bomem MB-120 instrument in which microcrystal clusters about 0.2 mm long and 0.02 mm thick were placed in a diamond-cell holder. The results for the two minerals are similar (Fig. 5). In the OH–H<sub>2</sub>O stretch region between 3000 and 3500 cm<sup>-1</sup>, barahonaite-(Al) has two strong absorption bands of similar amplitude, which are less well resolved in barahonaite-(Fe). The sharp, medium-strength band at ~1650 cm<sup>-1</sup> is assigned to bending vibrations of H<sub>2</sub>O, and the strong, sharp

band at ~1080 cm<sup>-1</sup> likely arises from As–OH interactions. The bands at ~980 and 840 cm<sup>-1</sup> are attributable to As–O stretching vibrations. Although the bands involving As interactions are at slightly lower wavenumbers in barahonaite-(Fe) relative to barahonaite-(Al), the opposite occurs for two of the three bands involving OH interactions.

Laser-Raman spectra of unpolished ~0.2 mm clusters of barahonaite-(Fe) and barahonaite-(Al) from the Dolores prospect were obtained with a Jobin Yvon T64000 instrument and an Ar laser at 514.5 nm. Barahonaite-(Fe) has a strong fluorescence at this frequency, resulting in a spectrum of low intensity, but no improvement was obtained at a frequency of 457.9 nm. The Raman spectra in the low-frequency region from 0 to 1200 cm<sup>-1</sup> are shown in Figure 6, wherein it is evident that the spectra for both minerals are similar. The band assignments in this region are like those given by Jambor *et al.* (2002) for cobaltarthurite.

### Compatibility index

The measured density of barahonaite-(Al) is 3.03 g/cm<sup>3</sup>, and K<sub>C</sub> derived from the electron-microprobe data

ranges from 0.201 to 0.210, averaging about 0.206. If it is assumed that  $n_{\beta}$  is 1.619, which would yield a  $2V_{\text{calc}}$  of  $-66^{\circ}$ , then  $n_{\text{mean}}$  is 1.618. Hence,  $K_{\text{P}}$  is 0.204 and the compatibility is 0.010 (superior). For barahonaite-(Fe),  $K_{\text{C}}$  for the listed analytical data (Table 1) is 0.218. If  $n_{\beta}$  is taken as 1.674, which is close to  $n_{\gamma}$  and yields a  $2V_{\text{calc}}$  of  $-57^{\circ}$ , mean  $n$  is 1.672. A density of  $3.0 \text{ g/cm}^3$  would give an index of compatibility of  $-0.026$  (excellent).

#### X-RAY DATA

That barahonaite-(Fe) and barahonaite-(Al) are related to the smolianinovite group was not recognized until late in the study because the  $22 \text{ \AA}$  line, which is the strongest one in the X-ray-diffraction pattern of smolianinovite, is not clearly resolved on 114-mm Debye-Scherrer films. An attempt to obtain the unit-cell parameters of barahonaite-(Al) by transmission electron microscopy (TEM) was unsuccessful because the mineral is beam-sensitive, and the axial lengths obtained by TEM were found to be too small to index the powder pattern. This instability is in accord with the indications that the barahonaite-type minerals are affected by the vacuum or the electron beam (or both) during electron-microprobe analysis.

A unit cell for barahonaite-(Al) was derived by manual trial-and-error indexing of the X-ray powder pattern. The indexing required that the longest axis be  $22 \text{ \AA}$ , and a subsequent check with a 57-mm camera, specially designed to show diffraction lines in the low- $2\theta$  region, confirmed that not only is a  $22 \text{ \AA}$  line present, it is the strongest line in the X-ray pattern. This, in turn, led to the discovery that the Gold Hill mineral might be related to barahonaite-(Al), and also led to the

later recognition of the similarity to the minerals of the smolianinovite group.

The X-ray powder data for barahonaite-(Fe) and barahonaite-(Al) are given in Table 2. The Debye-Scherrer X-ray patterns of barahonaite-(Al) from the Dolores prospect are sharper than those of the Gold Hill mineral and barahonaite-(Fe). The pattern of barahonaite-(Al) was initially indexed with  $a 9.972(2)$ ,  $b 22.44(7)$ ,  $c 5.272(8) \text{ \AA}$ ,  $\beta 92.9(1)^{\circ}$ ,  $V 1178(2) \text{ \AA}^3$ , and that of barahonaite-(Fe), with  $a 10.172(6)$ ,  $b 22.43(3)$ ,  $c 5.286(5) \text{ \AA}$ ,  $\beta 93.09(9)^{\circ}$ ,  $V 1204(2) \text{ \AA}^3$ , for which  $Z = 1$ . However, the  $c$ -axis length was subsequently doubled after indexing the X-ray diffractograms of vacuum-treated and heated barahonaite-(Al).

#### Vacuum and heat treatments

The reserved 2 mg of hand-picked barahonaite-(Al) from Utah, which was the split of the sample that had been used for the TG-DT analyses, was used to prepare an X-ray diffractogram. The same X-ray mount was then placed in a SEM chamber and was left under vacuum overnight. After rerunning the diffractogram, the mount was heated to  $135 \pm 5^{\circ}\text{C}$  in air for about  $1\frac{1}{2}$  h. The X-ray results for the untreated, vacuum-treated, and heated samples are shown in Figure 7, and the measured  $d$  values for the treated samples are given in Table 3. Comparison of the X-ray patterns indicates that the first peak in the diffraction pattern, indexed as 010 in barahonaite-(Fe) and barahonaite-(Al), decreases in intensity and  $d$  value, and that the first three peaks of the heated sample can be indexed as 010, 001, and 100. The resulting unit-cell dimensions are similar to those of the barahonaite minerals, except that the  $c$  axis

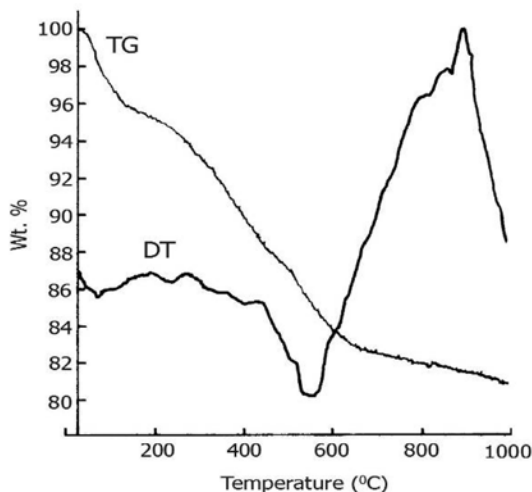


FIG. 4. TG and DT results for the Utah barahonaite-(Al).

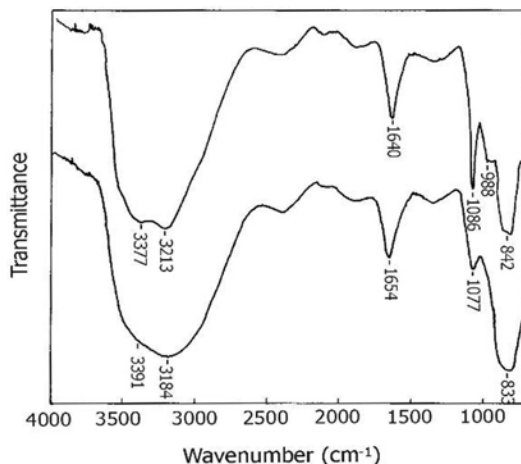


FIG. 5. Infrared spectra of barahonaite-(Al) from Spain (top) and barahonaite-(Fe).

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR BARAHONAITE-(Fe), BARAHONAITE-(Al) AND ATTIKAITE

barahonaite-(Fe), Spain				barahonaite-(Al), Spain				attikaite <sup>c</sup>			
<i>I</i> <sub>est</sub>	<i>d</i> <sub>meas</sub> Å	<i>d</i> <sub>calc</sub> Å	<i>hkl</i>	<i>I</i> <sub>est</sub>	<i>d</i> <sub>meas</sub> Å	<i>d</i> <sub>calc</sub> Å	<i>hkl</i>	<i>I</i> <sub>est</sub>	<i>d</i> <sub>meas</sub> Å	<i>d</i> <sub>calc</sub> Å	<i>hkl</i>
100	22.0 <sup>a</sup>	22.390	010	100	22.0 <sup>a</sup>	22.430	010	100	22.8	22.78	001
70	11.2	11.195	020	70	11.16	11.215	020	60	11.36	11.39	002
5	7.38	7.463	030	10	7.47	7.477,7.444	030,120	10	7.61	7.593	003
3	5.269	5.267	002	20	5.269	5.271,5.266	002,131				
20	5.068	5.072	200*	50	4.983	4.976	200*	90	5.01	5.005	200
5	4.689	4.681	112*	3	4.888	4.885	140				
				10	4.570 <sup>b</sup>	4.568	102*	10	4.55	4.582,4.556	202,005
3	4.489	4.491,4.478	141,050	10	4.478	4.476,4.473	112,141				
3	4.332	4.314	221*								
10B	4.138	4.153,4.121	221,051	20	4.147	4.143	230*	10	4.09	4.099	020
10	4.027	4.029	132*	20	4.013	4.012	132*				
10	3.712	3.710	212*	3	3.883	3.898	132				
3	3.404	3.412	052*	3	3.735	3.738	060				
20	3.345	3.350,3.344	023,310	25	3.655	3.659	212*				
				10	3.544	3.542	142*				
5B	3.167	3.168,3.164	301,251	45	3.333	3.332,3.328	250*,113	50	3.38	3.394,3.369	123,205
5	3.081	3.080	330*	3	3.082	3.085	321	10	3.12	3.141,3.116	221,215
				30	3.003	3.007	321*	10	3.06	3.063,3.055	311,222
				20	2.903	2.898	261*	10	2.906	2.915,2.895	125,117
				20	2.823	2.821	143*				
30B	2.763	2.762	053*	30	2.767	2.767	053*	70	2.780	2.786	026
				20	2.736	2.738	072*				
				25	2.654	2.657	172*	30	2.682	2.684	126
				3	2.594	2.594	271				
20	2.541	2.536	400*	35	2.493	2.492,2.488	090,400	50	2.503	2.503	400
5	2.496	2.499	114*								
3	2.447	2.450	280*	5	2.442	2.443	280*				
3	2.400	2.401	430*	3	2.366		several				
3	2.334	2.337	402*	5	2.325	2.327,2.325	431,224*				
5	2.290		several	5	2.280	2.284,2.281	204,112	20	2.292	2.291	404
3	2.251		several	5	2.238		several	10B	2.25	2.259,2.250	209,325
3	2.119		several								
5	2.092		several	10	2.208		several	10B	2.08	2.089,2.079	406,332
3	2.042		several	5	2.035		several				
5	1.976		several	3	1.961		several	10B	1.98		several
3	1.908		several	10	1.924	1.924,1.920	530*,084	10B	1.93		several
5	1.693		several	5	1.890		several				
3	1.671		several	3B	1.869		several				
3	1.627		several	3	1.807		several				
10	1.586		several	10B	1.766		several				
				5	1.724		several	10	1.738	1.741,1.741	341,239
								20	1.666		several
				10B	1.622		several				
				3	1.599		several				
				20	1.572		several	15	1.570		several

<sup>a</sup> Obtained with a modified 57.3 mm Debye-Scherrer camera. <sup>b</sup> Partly overlaps the strongest reflection of pharmacosiderite. Diffraction lines at 7.95 (10) and 3.25 (3) Å in the pattern of barahonaite-(Fe) are attributed to pharmacosiderite and have been omitted.

<sup>c</sup> Data from Chukanov *et al.* (2007), who gave additional indices for *d* values at 2.25 Å and lower. Lateral correlations in *d* values are interpretations from the current study.

\* Indices with an asterisk were used in the unit-cell refinements. Barahonaite-(Fe) was indexed with *a* 10.161(7), *b* 22.39(2), *c* 10.545(10) Å,  $\beta$  93.3(1)°; barahonaite-(Al) was indexed with *a* 9.964(3), *b* 22.43(1), *c* 10.555(6) Å,  $\beta$  92.76(6)°.



is doubled; for the vacuum-treated sample,  $a$  9.652(5),  $b$  18.586(9),  $c$  11.133(4) Å,  $\beta$  93.59(6)°, and for the heated sample  $a$  9.700(9),  $b$  18.46(2),  $c$  11.128(8) Å,  $\beta$  93.38(9)°. Although the results do not prove that the value for  $c$  obtained in the preliminary indexing of barahonaite-(Fe) and barahonaite-(Al) should also be doubled, to  $\sim 10$  Å, the enlarged cell has nonetheless been adopted (Table 2).

Chukanov *et al.* (2007) observed by infrared spectroscopy that the heating of attikaite (composition in

Table 1) to 140°C for 35 minutes resulted in the loss of all H<sub>2</sub>O, with only OH retained. The loss of H<sub>2</sub>O was accompanied by a reduction in cell volume. The indexed X-ray patterns of vacuum- and heat-treated barahonaite-(Al) also indicate a decrease in unit-cell volumes, to 1993(2) Å<sup>3</sup> and 1989(4) Å<sup>3</sup>, respectively. The decrease in volume is related principally to a substantial contraction in the length of the  $b$  axis, from 22.4 to  $\sim 18.5$  Å, which is only partly offset by a smaller increase in  $c$ , from 10.5 to 11.1 Å. The cell-volume decrease is in

TABLE 3. X-RAY POWDER DATA FOR BARAHONAITE-(Al) AFTER VACUUM AND HEAT TREATMENT, AND FOR HEATED ATTIKAITE

Barahonaite-(Al), vacuum				Barahonaite-(Al), heated				Attikaite, heated			
$l$	$d_{\text{meas}}$	$d_{\text{calc}}$	$hkl$	$l$	$d_{\text{meas}}$	$d_{\text{calc}}$	$hkl$	$l$	$d_{\text{meas}}$	$d_{\text{calc}}$	$hkl$
100	19.19	18.59	010	100	18.64	18.46	010	80	19.1	18.77	001
16	11.15	11.11	001	28	11.04	11.11	001				
32	9.646	9.63	100	35	9.62	9.68	100				
40	9.293	9.29	020	49	9.22	9.23	020	90	9.32	9.385	002
				39	8.60	8.575	110				
9	5.776		Acr	17	5.776		Acr				
18	5.624	5.623	121	36	5.623	5.625	121				
30	5.557	5.556	002	52	5.565	5.554	002				
31	4.942	4.949	$\bar{1}02$	57	4.947	4.946	$\bar{1}02$	100	5.01	5.008	200
20	3.545	3.544	231	35	3.548	3.550	042	40	4.39	4.418	202
6	3.480	3.484	$\bar{2}22$			3.550	231	30	4.10	4.106	020
5	3.233	3.241	$\bar{2}41$	12	3.248	3.236	$\bar{2}41$	70	3.75	3.762, 3.754	022, 005
9	3.182	3.182	123	26	3.186	3.184	123	20	3.57	3.530	213
		3.179	033			3.180	310	80	3.43	3.433, 3.424	023, 204
20	3.011	2.995	311	9	3.099	3.105	$\bar{3}11$	40	3.14	3.131	221
				34	3.014	3.011	311	40	2.970	3.008, 3.004,	222, 205,
										2.953	124
39	2.987	2.990	$\bar{2}13$	69	2.988	2.989	$\bar{2}13$	30	2.841	2.832	223
		2.984	061					70	2.788	2.806, 2.773,	116, 313,
										2.771	025
12	2.927	2.922	$\bar{2}42$	21	2.931	2.936	250	70	2.675	2.681, 2.670	007, 125
						2.930	160	10	2.563	2.566	321
14	2.806	2.812	242	25	2.809	2.813	242	50	2.503	2.504	400
37	2.776	2.778	004	64	2.777	2.777	004	40	2.375	2.383, 2.376,	231, 411,
										2.364	207
				8	2.607	several		10	2.161	2.160	135
5	2.530	2.527	124					20	2.083	2.086, 2.084,	009, 422,
										2.083	405
4	2.492	2.486	$\bar{1}34$					30	1.895	1.902, 1.900,	416, 240,
										1.890	241
5	2.252	2.254	421	12	2.245	2.245	180	40	1.783	1.789, 1.786,	237, 417,
										1.773	145
7	2.239	2.245	430	13	2.237	2.232	$\bar{4}31$	30	1.720	1.719, 1.719,	342, 434,
										1.719	2.1, 10
7	2.234	2.229	360			2.227	360	40	1.670	1.672, 1.669	427, 600
13	2.218	2.222	005	24	2.219	2.222	005	10	1.614		several
4	2.187	2.189	352	8	2.185	2.191	352	60	1.574		several
		2.184	244	9	2.167	2.167	361				
4	1.971	several		8	1.973	several					
8	1.919	several		16	1.921	several					
4	1.851	several		7	1.852	several					
		1.852	006			1.851	006				
5	1.772	several		11	1.773	several					
4	1.640	several		7	1.642	several					
				7	1.608	several					

Cobalt radiation,  $\lambda = 1.79026$  Å;  $d$  values in Å. Barahonaite-(Al) heated to 130°C. Vacuum-treated sample indexed with  $a$  9.652(5),  $b$  18.586(9),  $c$  11.133(4) Å,  $\beta$  93.59(6)°; heated sample indexed with  $a$  9.700(9),  $b$  18.46(2),  $c$  11.128(8) Å,  $\beta$  93.38(9)°.

Data for attikaite are from Chukanov *et al.* (2007); sample heated to 128°C; indexed with  $a$  10.016(5),  $b$  8.212(5),  $c$  18.77(1) Å. Lateral correlation (this study) of  $d$  values applies only to the first three entries ( $l = 80, 90, 100$ ). Acr: arsenocandallite.

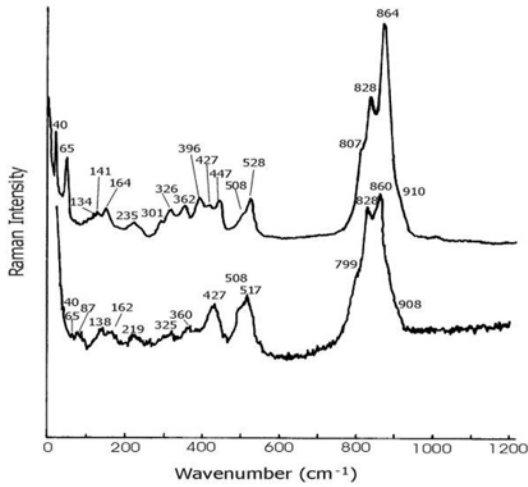


FIG. 6. Raman spectra of barahonaite-(Al) from Spain (top) and barahonaite-(Fe).

accord with the low-temperature loss in weight attributable to the release of loosely bound structural  $\text{H}_2\text{O}$ , as is observed in the TG-DT analyses (Fig. 4).

#### RELATIONSHIP TO THE SMOLIANINOVITE GROUP

Smolianinovite, a “grandfathered” valid species, is a poorly crystalline arsenate first reported to occur at Bou Azzer, Morocco (Yakhontova 1956). The mineral has since been recognized at several other localities, for which only an occurrence at Mt. Cobalt, Australia (Smith *et al.* 1977) has supporting quantitative chemical data. The formula of smolianinovite is generally given as  $(\text{Co}, \text{Ni}, \text{Mg}, \text{Ca})_3(\text{Fe}^{3+}, \text{Al})_2(\text{AsO}_4)_4 \cdot 11\text{H}_2\text{O}$ .

The IMA-approved mineral fahleite (Medenbach *et al.* 1988) was given the ideal formula  $\text{CaZn}_5\text{Fe}^{3+}_2(\text{AsO}_4)_6 \cdot 14\text{H}_2\text{O}$  [which could be generalized as  $(\text{Zn}, \text{Ca})_6\text{Fe}_2(\text{AsO}_4)_6 \cdot 14\text{H}_2\text{O}$ ] and was assigned to the newly constituted “smolianinovite group”, wherein smolianinovite became  $(\text{A}^{2+}, \text{Fe}^{3+}, \text{Al})_6\text{Fe}^{3+}_2(\text{AsO}_4)_6 \cdot n\text{H}_2\text{O}$ , with  $n = 18$  or 19 and with  $\text{Fe}^{3+}$  and Al in excess

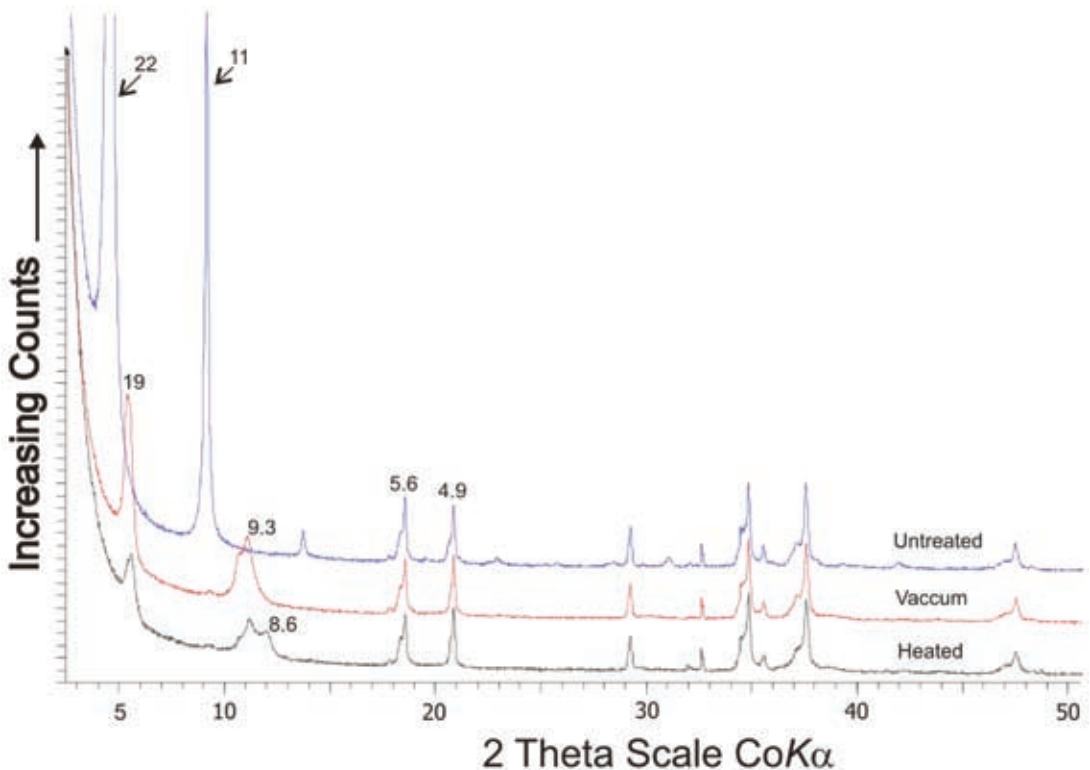


FIG. 7. X-ray diffractograms of untreated, vacuum-treated, and heated barahonaite-(Al) from Utah;  $d$  values (in Å) are given for some of the peaks (see Table 3).

of 2.00 *apfu* allocated to the A position in the formula. Other than composition, the grouping of fahleite and smolianinovite was strongly influenced by the similarity in X-ray powder patterns; both minerals are poorly crystalline, and a distinctive feature is that their X-ray patterns have only a few diffraction lines, all of which are broad and diffuse (Table 4). Indexing of the powder pattern of smolianinovite by Yakhontova *et al.* (1973) gave an orthorhombic unit-cell corresponding to that in Table 5. This unit cell does not satisfactorily index the powder patterns of barahonaite-(Fe), barahonaite-(Al),

and attikaite, all of which have many more X-ray reflections than appear for smolianinovite and fahleite.

The chemical compositions of the aforementioned minerals, except for attikaite (Table 1), are compared in Table 6 after calculation on the basis of  $XO_4 =$

TABLE 4. COMPARISON OF X-RAY POWDER DATA

Smolianinovite <sup>1</sup>		Fahleite <sup>2</sup>		Barahonaite-(Fe) <sup>3</sup>		Barahonaite-(Al) <sup>3</sup>		Attikaite <sup>3</sup>	
<i>l</i>	<i>d</i> (Å)	<i>l</i>	<i>d</i> (Å)	<i>l</i>	<i>d</i> (Å)	<i>l</i>	<i>d</i> (Å)	<i>l</i>	<i>d</i> (Å)
100	21.94	100	22	100	22.0	100	22.0	100	22.8
80	11.58	100	11	70	11.19	70	11.16	60	11.36
				20	5.07	50	4.98	90	5.01
60	3.30	80	3.2	20	3.35	45	3.33	50	3.38
50	2.92	50	2.9			30	3.00	10	2.91
				30	2.76	30	2.77	70	2.78
10	2.59			20	2.66	25	2.65	30	2.68
				20	2.54	35	2.49	50	2.50
								20	2.29
50	1.642	20	1.65			25B	1.66	20	1.66
20	1.486								

<sup>1</sup> Pattern has only seven lines, all diffuse (data from Yakhontova *et al.* 1973; ICDD43-0676). Similar results (six lines to a *d* of 1.50 Å) were obtained by Cuchel (1994) who, on the basis of qualitative EDS analysis, obtained  $Mg > Ca > Mn > Ni$  for the A-site cations, with no Co and no Al detected.

<sup>2</sup> Pattern has only five lines, all diffuse (Medenbach *et al.* 1988; ICDD42-1417).

<sup>3</sup> Only the strongest lines are listed.

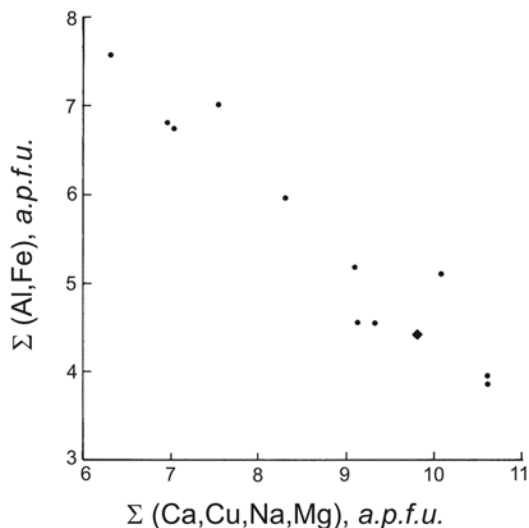


FIG. 8. Variation in (Ca,Cu,Na,Mg) versus (Fe,Al) (*apfu*) in the barahonaite-(Fe) – barahonaite-(Al) series. The diamond represents the composition given in Table 1 for barahonaite-(Fe).

TABLE 5. COMPARISON OF DATA FOR SMOLIANINOVITE, FAHLEITE, ATTIKAITE, BARAHONAITE-(Al) AND BARAHONAITE-(Fe)

	Smolianinovite	Fahleite	Attikaite	Barahonaite-(Al)	Barahonaite-(Fe)
Reported formula <sup>a</sup>	(Co,Ni,Mg) <sub>3</sub> CaFe <sub>2</sub> (AsO <sub>4</sub> ) <sub>4</sub> •11H <sub>2</sub> O	Zn <sub>2</sub> CaFe <sub>2</sub> (AsO <sub>4</sub> ) <sub>4</sub> •11H <sub>2</sub> O	Cu <sub>2</sub> Cu <sub>2</sub> Al <sub>2</sub> (AsO <sub>4</sub> ) <sub>4</sub> (OH) <sub>4</sub> •2H <sub>2</sub> O		
ICDD #	43-0676	42-1417			
System	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
<i>a</i> (Å)	11.61	11.3	10.01	9.964	10.161
<i>b</i> (Å)	21.94	22	8.199	22.43	22.39
<i>c</i> (Å)	6.49	6.5	22.78	10.555	10.545
β (°)				92.76	93.3
<i>V</i> (Å <sup>3</sup> )	1653	1616	1870	2356	2395
<i>Z</i>	3	3	4	2	2
<i>D</i> <sub>meas</sub>	2.05–2.15 <sup>b</sup>	not determined	3.2	3.03	not determined
<i>D</i> <sub>calc</sub>	3.3	3.39	3.356	2.89–3.06	2.93–3.11
Indices of refraction					
α		1.628	1.642	1.612	1.664
β	1.625	1.631	1.644		~γ
γ		1.656	1.644	1.622	1.677
2 <i>V</i>		39° (calc.)	10° (meas.)		45–80°

<sup>a</sup> Formula as reported by ICDD (International Centre for Diffraction Data) for smolianinovite and fahleite.

<sup>b</sup> *D*<sub>meas</sub> = 3.05 g/cm<sup>3</sup> for smolianinovite from Mt. Cobalt, Australia (Smith *et al.* 1977).

8. Regardless of the number of trivalent cations in barahonaite-(Fe) and barahonaite-(Al), the sum of *A* + *B* is about 14 *apfu*. The corresponding sum in smolianinovite and fahleite is lower, ranging from about 11.0 to 12.7 *apfu* (Table 6). The reason for the difference is not known, and an assumption that a cation, such as Na, has gone undetected would only be convenient speculation. Consequently, the inclusion of barahonaite-(Fe) and barahonaite-(Al) in the smolianinovite group remains in doubt despite the X-ray indications that all follow a basically similar crystal-structure motif. Numerous electron-microprobe compositions of the barahonaite-series minerals have been obtained, and these show, appropriately, that as  $\Sigma(A^{1+} + A^{2+})$  increases, the amount of (Fe,Al) at *A* decreases (Fig. 8). The trend is well defined for the barahonaite series, but the published compositions of smolianinovite and fahleite do not fit well with the trend.

With regard to the extent of substitution of (Fe,Al) that can be accommodated at *A* in the formula, barahonaite-(Al) and barahonaite-(Fe) have Ca as the dominant cation in *A*, but Figure 8 shows that some compositions have sufficient Fe<sup>3+</sup> to make it the dominant cation at both *A* and *B*. Thus, the indication is that a Fe<sup>3+</sup>-dominant analog of barahonaite-(Fe) exists. Moreover, although the formula of smolianinovite is generally reported as Co-dominant in *A*, one of the compositions reported in the original description by Yakhontova (1956) is Ni-dominant (Table 6). As a further indication of compositional variation, the qualitative analysis of Cuchet (1994) of "smolianinovite" from Switzerland showed a predominance of Mg and an absence of Co, and the suggested occupancy at *A* was given as (Mg,Ca,Mn,Ni). It is evident that much work remains to be done with regard to the characterization, definition, and nomenclature of smolianinovite-type minerals.

#### RELATIONSHIP TO ATTIKAITE

The recently described new species attikaite (Chukanov *et al.* 2007) is almost identical to barahonaite-(Al) in macroscopic appearance, and there are also similarities in chemical composition (Table 1) and in X-ray powder-diffraction pattern (Table 2). As with barahonaite-(Al) and barahonaite-(Fe), it has not been possible to obtain single-crystal data for attikaite; thus, unit cells of all of the minerals have been derived by indexing of the X-ray powder patterns.

The simplified formula of attikaite is given by Chukanov *et al.* (2007) as Ca<sub>3</sub>Cu<sub>2</sub>Al<sub>2</sub>(AsO<sub>4</sub>)<sub>4</sub>(OH)<sub>4</sub>•2H<sub>2</sub>O, which if recast to a barahonaite-type formula, becomes (Ca<sub>6</sub>Cu<sub>4</sub>Al<sub>2</sub>) $\Sigma_{12}$ Al<sub>2</sub>(AsO<sub>4</sub>)<sub>8</sub>(OH)<sub>8</sub>•4H<sub>2</sub>O. Thus, the most significant compositional difference between attikaite and barahonaite-(Al) is the much higher content of H<sub>2</sub>O in barahonaite-(Al). However, the combination of X-ray and TG-DT analyses indicates that even the low-temperature, early-released H<sub>2</sub>O from barahonaite-(Al) is structure-related rather than absorbed (Fig. 7).

The X-ray powder-diffraction patterns of the barahonaite minerals have similarities to those of attikaite and the smolianinovite group insofar as all have strong diffraction peaks at roughly the same *d* values (Table 4). Barahonaite-(Al), barahonaite-(Fe), and attikaite have the greatest number of diffraction peaks, and the differences among the three minerals are pronounced only if all of the diffraction peaks in the patterns are included for comparison (Table 2). Whereas the powder pattern of attikaite can be indexed with an orthorhombic unit-cell (Chukanov *et al.* 2007), the mismatches and especially the additional peaks in the X-ray pattern of barahonaite-(Al) require the adoption of a monoclinic cell to satisfactorily index its pattern. For heated barahonaite-(Al) and attikaite, the X-ray powder patterns are dissimilar. Likewise, the X-ray pattern of vacuum-treated barahonaite-(Al) does not match that of

TABLE 6. COMPOSITION VARIATIONS IN SMOLIANINOVITE-LIKE MINERALS

	Smolianinovite		Fahleite		Barahonaite	Barahonaite	
					-(Al)	-(Fe)	
	Morocco <sup>1</sup>	Mt. Cobalt,	Tsumeb,		Spain <sup>4</sup>	Spain	Spain
	a	b	Australia <sup>2</sup>	Namibia <sup>3</sup>		Avg.	Spot 6.4
Na <sub>2</sub> O wt.%	—	—	—	—	1.65	2.07	1.24
MgO	3.10	3.05	1.31	—	—	0.14	—
CaO	3.69	4.15	5.10	4.0	15.71	12.96	10.13
MnO	—	—	—	0.5	—	—	—
NiO	7.18	9.19	0.42	—	—	—	—
CoO	8.01	9.02	14.88	—	—	—	—
CuO	—	—	—	—	14.59	12.41	9.01
ZnO	—	—	—	26.2	—	—	—
Al <sub>2</sub> O <sub>3</sub>	1.50	2.21	2.36	—	9.52	1.71	3.51
Fe <sub>2</sub> O <sub>3</sub>	11.80	10.18	12.01	10.2	0.10	13.78	19.27
P <sub>2</sub> O <sub>5</sub>	—	—	—	—	0.35	0.42	—
As <sub>2</sub> O <sub>5</sub>	41.88	39.29	43.96	43.6	42.16	41.18	39.99
SO <sub>3</sub>	—	—	—	—	1.24	0.29	0.14
SiO <sub>2</sub>	0.75	0.85	0.0	—	0.14	0.33	0.28
H <sub>2</sub> O	21.79	22.32	20.83	[15.5]	[14.49]	[14.01]	[16.41]
Cl	—	—	—	—	0.06	0.91	0.03
O-Cl	—	—	—	—	0.01	0.21	0.01
Sum	99.7	100.26	100.87	100	100	100	100
Na <i>apfu</i>	—	—	—	—	1.093	1.431	0.903
Mg	1.633	1.701	0.680	—	—	0.074	—
Ca	1.397	1.663	1.902	1.504	5.752	4.951	4.078
Mn	—	—	—	0.149	—	—	—
Ni	2.040	2.764	0.118	—	—	—	—
Co	2.269	2.705	4.153	—	—	—	—
Cu	—	—	—	—	3.766	3.342	2.557
Zn	—	—	—	6.789	—	—	—
Al	0.625	0.974	0.968	—	3.835	0.719	1.554
Fe	3.137	2.865	2.114	2.694	0.026	3.698	5.449
$\Sigma$	11.101	12.672	10.967	11.136	14.472	14.215	14.541
P	—	—	—	—	0.101	0.127	—
As	7.736	7.682	8.000	8.000	7.533	7.678	7.856
S	—	—	—	—	0.318	0.078	0.039
Si	0.265	0.318	—	—	0.048	0.118	0.105
$\Sigma$	8.001	8.000	8.000	8.000	8.000	8.001	8.000
Cl	—	—	—	—	0.035	0.550	0.019
OH	1.701	4.867	2.047	0.964	7.947	6.823	11.097
$\Sigma$	1.701	4.867	2.047	0.964	7.982	7.373	11.116
H <sub>2</sub> O	24.82	25.40	23.15	17.66	12.54	13.25	15.01

The formula are calculated on the basis of XO<sub>4</sub> = 8 per formula unit. <sup>1</sup> Yakhontova (1956); two compositions are shown, those with the highest and lowest values of  $\Sigma$  cations. <sup>2</sup> Smith *et al.* (1977). <sup>3</sup> Medenbach *et al.* (1988). <sup>4</sup> See also the composition of attikaite in Table 1.

attikaite. Thus, the conclusion is that barahonaite-(Al) and attikaite are not the same species even though, as with the smolianinovite group, they may share a similar crystal-structure topology.

#### ACKNOWLEDGEMENTS

We thank Serveis Científicotècnics of the University of Barcelona for providing instrumentation and technical assistance. Graham Carpenter of CANMET did the TEM investigation, and J.H.G. Laflamme provided substantial assistance, which included SEM images and some of the early electron-microprobe analyses. Guidance by Ernst Burke, Chairman of the CNMNC, the reviews by Carl A. Francis and Jason Burt, and the editorial comments by R.F. Martin are much appreciated.

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Received July 17, 2007, revised manuscript accepted November 19, 2007.

