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THE DIVERSITY AND OCCURRENCE OF POTASSIUM-DOMINANT AMPHIBOLES

FRANK K. MAZDAB[§]

Center for Solid State Science, Arizona State University, Tempe, Arizona 85287, U.S.A.

ABSTRACT

Currently, the Commission on New Minerals and Mineral Names (CNMMN) of the International Mineralogical Association (IMA) recognizes seven amphibole species where potassium is the dominant *A*-site cation. These include potassic-ferrisadanagaite, potassic-fluororichterite, potassic-magnesiosadanagaite, potassicpargasite, potassicsadanagaite, potassic-chloropargasite and potassicleakeite. However, as a result of an evaluation of compositions of Cl-bearing amphibole samples from iron-oxide-rich ore systems and a comparison with data in the reviewed literature, fourteen additional naturally occurring potassium-dominant amphiboles can be justified from selected published chemical data using recommended protocols for normalization. In keeping with accepted amphibole nomenclature, these new amphibole end-members would be "potassichastingsite", "potassic-chlorohastingsite", "potassic-ferropargasite", "potassic-chloro-ferropargasite", "potassic-aluminosadanagaite", "potassic-chlorosadanagaite", "potassic-chloro-ferro-edenite", "potassicrichterite", "potassic-ferrorichterite", "potassic-fluoro-magnesiokatophorite", "potassic-ferritaramite", "potassic-magnesio-arfvedsonite", "potassic-fluoro-magnesio-arfvedsonite" and "potassickornite". In several of the potassium-dominant amphiboles evaluated, chlorine is an important OH-site component, even where it is not the dominant anion, and the optional modifier "chlorian" is appropriate. Indeed, various species of both Cl-rich and K-rich ferropargasite and hastingsite (both *sensu lato*) are characteristic amphiboles of certain iron-oxide-rich hydrothermal systems associated with alkali–chloride metasomatism. At one locality, another new chlorine-dominant amphibole, although lower in potassium, seems present: potassian "chlorosadanagaite". In addition to mineralization related to hypersaline fluids, the "potassic-" amphiboles are otherwise widespread in diverse igneous, metamorphic, and metasomatic environments. It is hence desirable and justifiable, notably for those cases where results of chemical analyses are accompanied by data on crystallographic and physical properties, to confer species status to these amphiboles.

Keywords: potassium-dominant amphiboles, amphibole nomenclature, chemical data, normalization routines, alkali–chloride metasomatism, hypersaline fluids.

SOMMAIRE

La Commission des nouveaux minéraux et des noms de minéraux (CNMMN) de l'Association Internationale de Minéralogie (IMA) reconnait sept espèces d'amphibole dans lesquelles le potassium est prédominant au site *A*. Ce sont: potassic-ferrisadanagaïte, potassic-fluororichtérite, potassic-magnésiosadanagaïte, potassicpargasite, potassicsadanagaïte, potassic-chloropargasite et potassicleakeite. Par contre, comme résultat d'une évaluation des compositions d'amphiboles contenant du

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[§] *Present address*: USGS–SUMAC Ion Probe Laboratory, Green Building, 367 Panama Mall, Stanford University, Stanford, California 94305, U.S.A. *E-mail address*: fmazdab@usgs.gov

chlore, provenant de systèmes minéralisés en oxydes de fer, et d'une comparaison avec les données dans la littérature, on peut justifier quatorze nouvelles espèces d'amphibole à dominance de potassium en utilisant les protocoles recommandés pour la normalisation. Ceux-ci se nommeraient, en termes du schéma de nomenclature accepté, "potassichastingsite", "potassic-chlorohastingsite", "potassic-ferropargasite", "potassic-chloro-ferropargasite", "potassic-aluminosadanagaïte", "potassic-chlorosadanagaïte", "potassic-chloro-ferro-edenite", "potassicrichterite", "potassic-ferrorichterite", "potassic-fluoro-magnésiokatophorite", "potassic-ferritaramite", "potassic-magnésio-arfvedsonite", "potassic-fluoro-magnésio-arfvedsonite" et "potassickornite". Dans plusieurs cas, le chlore est un composant important du site OH, même où il n'y est pas l'anion prédominant, et le qualificatif "chlorien" semblerait approprié. En fait, plusieurs espèces de ferropargasite et de hastingsite riches en K et en Cl (*sensu lato* dans les deux cas) seraient caractéristiques de certains systèmes hydrothermaux enrichis en oxydes de fer et associés à une métasomatose alcaline et chlorée. A un endroit, une autre amphibole nouvelle à dominance de Cl a été repérée, quoique sa teneur en K est plus faible: "chlorosadanagaïte" potassienne. En plus des exemples associés à la minéralisation causée par une phase fluide hypersaline, les amphiboles susceptibles de porter le préfixe "potassic-" sont aussi répandues dans les roches ignées, métamorphiques, et métasomatiques diverses. Il est donc souhaitable et justifiable, surtout là où les résultats d'analyses chimiques sont déjà accompagnées de données cristallographiques et où les propriétés physiques sont connues, d'attribuer le statut d'espèce à ces amphiboles.

(Traduit par la Rédaction)

Mots-clés: potassium-dominant amphiboles, amphibole nomenclature, chemical data, normalization routines, alkali–chloride metasomatism, hypersaline fluids.

INTRODUCTION

Amphiboles (general composition $A_{0-1}(M4)_2[(M1)_2(M2)_2(M3)]T_8O_{22}X_2$) are a chemically variable group of chain silicates with almost 100 recognized end-members (Mandarino 1999, 2001). The compositional diversity of the group arises from the large number of possible substitutions among the major cation and anion sites. Within such a large and complex group, the proliferation of species names has the potential to become confusing and unwieldy. Hence, to address nomenclature issues associated with the amphibole group, the Subcommittee on Amphiboles of the Commission on New Minerals and Mineral Names (CNMMN) proposed a set of guidelines to simplify the naming of amphiboles and to define the use of prefixes and modifiers more precisely (Leake *et al.* 1997). In addition, a new report on amphibole nomenclature, warranted by the discovery of several new lithium-rich amphiboles, provides additions and revisions to the Leake *et al.* (1997) guidelines (Leake *et al.* 2003). These most recent reports, intended to be used in conjunction, replace and update an earlier protocol concerning the nomenclature of amphiboles (Leake 1978).

Although the occurrences of potassium-rich amphiboles are well documented [*e.g.*, see Deer *et al.* (1997) for an overview], and potassium-rich compositions are accommodated in all of the recent nomenclature schemes as prefixes ["potassium-" (Leake 1978) and "potassic-" (Leake *et al.* 1997)], the formal recognition of many potassium-rich amphiboles as valid mineral species has been slow to follow. It is the focus of this paper to address some of the analytical and historical issues associated the nomenclature and species status of the potassium-rich amphiboles, and to provide an overview of occurrences and geochemical diversity.

BACKGROUND INFORMATION

The underlying structure of the Leake *et al.* (1997) nomenclature scheme is that a root name is assigned to each heterovalent substitution at the T, C (= $M1$, $M2$, $M3$), B (= $M4$), A, and X sites. Thus, dominant substitutions such as Al^{3+} for Si^{4+} at T, alkali metals for a vacancy at A, Na^+ for Ca^{2+} at B, Li^+ or a trivalent cation for a divalent cation at the M sites, and O for (OH + F + Cl) at X each define distinct "root names". These root names are then further modified by a prefix denoting important homovalent substitutions, such as Mg^{2+} for Fe^{2+} and Al^{3+} for Fe^{3+} at the M sites, and F^- for OH^- at X. The combination of the prefix and the root name make up the species name. Unlike Leake (1978), Leake *et al.* (1997) explicitly noted that prefixes are an integral part of the species name. Despite several minor inconsistencies in the scheme (*e.g.*, see the discussion on the nomenclature of winchite and other ambiguous end-members in Sokolova *et al.* 2001), the Leake *et al.* (1997) protocol is both elegant and widely used.

One homovalent substitution observed in some amphiboles is K for ^{A}Na. Whereas small amounts of potassium are reported in many amphiboles that are analyzed, those with K as an abundant or dominant A-site cation are much less frequently noted. In addition to being less common, potassium-dominant ("potassic-") amphiboles [where K > 0.50 *apfu* (atoms per formula unit) at the A site] also appear to have less species-diversity than the A-site-filled amphiboles as a whole, on the basis of an inventory of currently recognized species of amphibole. To date, among the 49 amphiboles defined with (Na + K) occupancy at the A site, only seven are potassium-dominant (Grice & Ferraris 2000, 2001, 2002, 2003, Mandarino 1999, Matsubara *et al.* 2002). These include potassic-ferrisadanagaite, potassic-fluororichterite, potassic-magnesiosadanagaite, potassicpargasite, potassicsadanagaite, potassic-chloropargasite and potassicleakeite.

However, the limited number of *formally* recognized species of potassium-dominant amphibole may not be an accurate reflection of the actual diversity of such species. During a study in which I characterized the silicate assemblages from a number of iron-oxide-rich hydrothermal systems, I identified several examples of potassium-bearing, chlorine-bearing, and rare-transition-metal-enriched (*e.g.*, scandium, vanadium) amphiboles, and some of these, although nameable by the Leake *et al.* (1997) scheme of nomenclature, do not correspond to currently defined potassium-dominant species. Furthermore, an evaluation of compositions of potassium-dominant amphiboles compiled by Deer *et al.* (1997) and taken from other sources demonstrates that (1) K-rich amphiboles span a variety of "root name" (*i.e.*, heterovalent exchange) compositions within the calcic, sodic-calcic, and sodic amphibole subgroups, (2) these amphiboles occur in diverse geological settings, and (3) the use of chemical modifiers and species names were inconsistent prior to Leake *et al.* (1997), resulting in a limbo for recognition of potassium-dominant amphibole species. Consequently, several of the potassium-rich amphiboles compiled by Deer *et al.* (1997), as well as numerous compositions from other sources, normalize to formulas not represented by currently defined species of amphibole.

The normalization of amphibole analytical data presents an additional complication to the practical application of nomenclature. In modern routine petrographic studies, minerals are almost exclusively characterized by electron probe micro-analysis (EPMA), a procedure with which one cannot measure concentrations of H or Li, nor differentiate between multiple oxidation states of the same element, most commonly iron. Even in samples where Li is absent and H may be stoichiometric, the calculated $Fe^{3+}/\Sigma Fe$ value may differ markedly from the true ratio simply because by default, the calculation is typically only a reflection of the overall cumulative analytical uncertainty. In samples poor in iron, the error in $Fe^{3+}/\Sigma Fe$ may be proportionately large, but the effect on nomenclature may be insignificant if, for example, $Mg >> Fe^{2+}$ and $^{VI}Al >> Fe^{3+}$, irrespective of the actual ratio. Similarly, in very Fe-rich samples, the error in $Fe^{3+}/\Sigma Fe$ may be relatively small, and at the same time the effect on nomenclature may also be small if $Fe^{2+} >> Mg$ and $Fe^{3+} >> {}^{VI}Al$. It is with amphiboles where $Mg \approx Fe^{2+}$ or $^{VI}Al \approx Fe^{3+}$ that compositions may potentially straddle several species boundaries and are most sensitive to estimates of $Fe^{3+}/\Sigma Fe$. Furthermore, as the *A* site in amphiboles commonly is not fully occupied, even calculation of $Fe^{3+}/\Sigma Fe$ does not result in a unique estimate as it would with typical pyroxenes, garnets, and other minerals usually without vacancies. Although EPMA cannot provide a definitive analytical $Fe^{3+}/\Sigma Fe$ value, utilizing different protocols for the normalization of results of a high-quality analysis can provide good upper and lower bounds for the average oxidation state of Fe in amphiboles, and result in a reasonable formula. Schumacher (1997) specifically described the problem of estimating the proportion of ferric iron in amphiboles and provides worked examples of the procedures.

OVERVIEW OF ANALYTICAL DATA AND NORMALIZATION ROUTINES

Selection of potassium-dominant amphiboles

Deer *et al.* (1997) provided a compilation of 267 analyzed amphibole samples in which (Na + K) > 0.50 *apfu* at the *A* site. Of these, 27 show K > 0.50 *apfu*, although ten of these datasets could not be normalized using any available protocol without violating charge-balance constraints or significantly over- or underfilling nominal site-occupancies; hence these were not further treated in this study. The remaining 17 samples [along with an additional one from Deer *et al.* (1997) in which K = 0.478 *apfu*, one from Mazdab (2001), and one of a potassium-dominant amphibole analyzed for this study] are representative of twenty diverse geological environments, localities, and "root name" compositional variants (Table 1).

Compositional data for all 20 amphiboles are given in Table 2. The data are entered exactly as in Deer *et al.* (1997), except for a presumed transposition of H_2O^+ and H_2O^- with sample 22–15. H_2O and Fe_2O_3 contents in Table 2 are also those from Deer *et al.* (1997), except where noted.

Over the course of this investigation, normalizations of numerous compositions of additional amphibole samples were collected from the literature to compare with and contrast to those compiled in Deer *et al.* (1997). Details of these are provided in the discussion and tables of data. In many of the examples from the literature, authors have normalized to end-member compositions already represented by samples compiled by Deer *et al.* (1997). However, in two instances, new end-member amphiboles *not* represented by compositions in Deer *et al.* (1997) were identified: an additional new potassium- and chlorine-dominant amphibole ("potassic-chlorosadanagaite") and another new chlorine-dominant amphibole ("chlorosadanagaite"), from the data of Kullerud & Erambert (1999), and "potassic-ferrorichterite", from the data of Hogarth (1997). Although reported herein, detailed evaluations of these analytical data are not included in the text, solely in an attempt to limit the total number of examined datasets to a manageable number. Nonetheless, normalization criteria identical to those applied to the samples from the Deer *et al.* (1997) compilation were used for these additional samples.

Normalization routines

To demonstrate species diversity among the potassium-dominant amphiboles, it is first necessary to show that any derived formula is effectively constant within acceptable tolerances and is not simply a function of the normalization scheme chosen. It follows then that nominally the species name should be independent of the normalization technique, except in limited instances where a composition lies on one or more boundaries in the system of nomenclature.

To this end, tentative stoichiometries for the compositions from Table 2 were calculated using each of the normalization protocols summarized in Table 3. The details of these normalization protocols are given in both Schumacher (1997) and in Spear (1993, p. 101-105). Ideally, results were considered acceptable if they conform to the following charge-balance and site-occupancy constraints: charge balance = 0; 7.995 *apfu* < Σ(*T*-site cations) < 8.005 *apfu*; 4.995 *apfu* < Σ(*C*-site cations) < 5.005 *apfu*; 1.995 *apfu* < Σ(*B*-site cations) < 2.005 *apfu*, and Σ(*A*-site cations) < 1.005 *apfu* (the flexibility in the allowable site-occupancy is taking into account any rounding errors). Owing to variations in the quality of published data, there were a few cases where application of seemingly appropriate routines for normalization did not result in acceptable site-occupancies (based on the above criteria). Indeed, for a few samples, no normalization protocol yielded acceptable results, yet the calculated stoichiometries generally deviated only slightly from nominal site-occupancies (<1% in the *T*, *C*, or *B* sites, and <4% in the *A* site; see below). These compositions are considered of marginal reliability but still useable in demonstrating general diversity of spe-

TABLE 1. K-DOMINANT AMPHIBOLES COMPILED FROM DEER *et al.* (1997) AND THIS STUDY*

sample number**	DHZ¶	locality	geological occurrence listed
13-33	"chloro potassic ferro-edenite"	Willroy mine, Manitouwadge mining camp, Ontario, Canada	calc-silicate rock
14-25	"potassium pargasite"	Tiree, Argyllshire, Scotland, U.K.	inclusion in marble in gneiss
14-57	chlorine-rich "potassium ferro-pargasite"	Sesia–Lanzo, western Alps, Italy	marble
15-20	"chloro-potassium hastingsite"	Airport Hill, Visakhapatnam, India	granodioritic charnockite
15-22	"chloro-potassium hastingsite"	Dashkesan, Azerbaijan	skarn in porphyritic gabbro
15-31	"chloro-potassium hastingsite"	Dashkesan, Azerbaijan	skarn in porphyritic gabbro
15-39	hastingsite	Pike's Peak, Colorado, U.S.A.	quartz syenite
15-40	magnesian "potassic hastingsite"	Cape Omega, Prince Olav Coast, East Antarctica	calc-silicate pod in hornblende gneiss
15-41	subsilicic magnesian "potassic hastingsite"	Daruma Rock, Prince Olav Coast, East Antarctica	calc-silicate pod in migmatitic hornblende-biotite gneiss
16-1	titanian "potassium alumino-sadanagaite"	Yuge Island, Japan	vesuvianite – spinel – titanite skarn
16-2	titanian "potassium alumino-magnesio-sadanagaite"	Myojin Island, Japan	titaniferous aluminous diopside vesuvianite – spinel – titanite skarn
16-4	"potassium sadanagaite"	Yuge Island, Japan	vesuvianite – spinel titanite skarn
22-5	"potassium fluoro-richterite"	Bufa del Diente aureole, northeastern Mexico	amphibole – diopside metachert band in marble
22-15	richterite	Khibina massif, Kola Peninsula, Russia	lujavrite pegmatite
26-3	"potassium ferri-taramite"	southwestern Tanzania	syenite-gabbro
32-5	kornite	Wessels mine, Kalahari, South Africa	Mn ore deposit
33-2	potassian "fluor magnesio-arfvedsonite"	Gatineau area, Quebec, Canada	vein in quartzite and biotite schist
33-7	"potassic magnesio-arfvedsonite"	Pendennis Point, Cornwall, U.K.	minette
A	chlorian "potassic-ferro-pargasite"	Burguillos del Cerro, Spain	cobaltian löllingite – uraninite – allanite calc-silicate "skarn"
C	arfvedsonite	Kola Peninsula, Russia	kakortokite pegmatite

* Original references for these compositions are provided in Table 2. ** Sample numbers consist of the number of the table and entry number from Deer *et al.* (1997) (*i.e.*, sample 13-33 is from Table 13, entry #33). Samples A has been previously described in Mazdab (2001); the analytical data for sample C were obtained for this study.
¶ DHZ: Deer *et al.* (1997) name (including chemical modifiers).

TABLE 2. REPORTED COMPOSITIONS FOR AMPHIBOLES IN THIS STUDY

sample	13-33	14-25	14-57	15-20	15-22	15-31	15-39	15-40	15-41	16-1	16-2	16-4	22-5	22-15	26-3	32-5	33-2	33-7	A	C
SiO_2 wt%	39.17	41.72	36.77	35.60	36.13	33.90	37.02	39.43	36.58	30.2	32.1	33.5	57.37	50.98	38.56	56.06	54.80	53.49	38.18	50.62
TiO_2	0.08	0.81	0.25	1.36	0.30	1.01	0.68	1.03	1.65	4.0	3.2	2.1	0.43	1.23	0.96		0.15	3.36	0.06	2.87
Al_2O_3	7.37	15.86	12.28	13.57	10.22	11.57	11.95	14.31	16.12	24.8	22.0	19.7	0.03	2.69	10.31	0.00	0.17	0.23	11.44	2.08
Cr_2O_3	0.02			0.18				0.02	0.01								0.07		0.00	0.00
Fe_2O_3	1.75	3.36	[3.02]		7.60	8.90		9.88					0.48	4.71	13.12	[4.93]	9.84		[2.37]	[3.04]
FeO	30.11	6.03	[24.93]	28.18	19.99	23.01	31.07	8.38	17.92	[15.2]	[13.7]	[17.8]	3.00	10.29	18.72		2.61	[12.83]	[26.86]	[10.04]
MgO	0.55	14.14	2.20	3.98	3.63	1.81	0.43	9.02	7.97	6.6	8.0	6.4	21.62	13.26	1.24	10.03	17.44	13.58	1.99	15.68
MnO	1.30	0.12	0.19	0.00	0.43		1.92	0.45	0.17	0.1	0.1	0.5	0.16	0.75	1.91		0.11	0.35	0.31	0.55
CaO	11.31	12.92	10.67	8.86	10.83	11.16	11.18	12.23	12.31	12.3	12.5	11.9	5.63	4.91	5.78	0.00	2.37	1.22	11.50	5.98
Na_2O	0.54	1.42	0.96	0.64	1.24	0.74	1.54	0.96	0.20	1.0	0.7	1.2	5.39	5.78	4.71	7.61	6.37	7.03	1.13	5.06
K_2O	2.91	2.60	3.59	2.48	2.84	3.34	2.62	3.07	4.55	3.7	3.8	3.1	3.76	3.14	2.73	3.56	3.44	3.81	2.68	3.15
F	0.33	0.16	0.00	1.00				0.20	0.23				2.72	1.47	0.30		2.33		0.00	2.72
Cl	4.73	0.46	4.09	4.18	7.24	4.95	0.59	0.10	0.03						0.15				2.38	0.00
H_2O+		0.85	[0.76]	[1.00]	1.05									1.50?	1.66	[2.68]	0.99		[1.22]	[0.78]
other*		0.06			0.21								0.15	0.21		15.13	0.05		0.12	0.52
subtotal	100.14	100.51	99.71	101.03	101.93	100.39	99.00	99.08	97.74	97.9	96.1	96.2	100.75	100.95	100.15	100.00	100.74	95.90	100.23	103.09
O=F,Cl	-1.20	-0.18	-0.92	-1.36	-1.63	-1.12	-0.13	-0.11	-0.11				-1.15	-0.61	-0.16		-0.98		-0.54	-1.14
Total	98.94	100.33	98.79	99.67	100.30	99.27	98.87	98.97	97.63	97.9	96.1	96.2	99.59	100.34	99.99	100.00	99.76	95.90	99.69	101.95
Ref., notes	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(8)	(9)	(9)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)

Except for samples A and C, Fe_2O_3, FeO, and H_2O are those values reported in Deer *et al.* (1997), whether measured or calculated. For samples A and C, these values are calculated using charge balance and stoichiometry constraints from measured electron-microprobe (EPMA) data. Values in brackets are specifically identified as calculated from EPMA data. * Details on other elements are included in "Ref., notes", which follow: (1) Pan & Fleet (1992); (2) includes 0.02 wt% Li_2O, Hallimond (1947); (3) Castelli (1988); (4) Kamineni *et al.* (1982); (5) includes 0.10 wt% P_2O_5 and 0.11 wt% SO_3, Krutov (1936); (6) Krutov (1936), Jacobson (1975); (7) Barker *et al.* (1975); (8) Shiraishi *et al.* (1994); (9) Shimazaki *et al.* (1984); (10) includes 0.15 wt% V_2O_3, Heinrich (1994); (11) includes 0.21 wt% V_2O_5, Dudkun *et al.* (1964); (12) Brock *et al.* (1964); (13) includes 13.17 wt% Mn_2O_3 and 1.96 wt% Li_2O, Armbruster *et al.* (1993); (14) includes 0.07 wt% Cr_2O_3, 0.03 wt% BaO and 0.02 wt% SrO, Hogarth *et al.* (1987); (15) Hall (1982); (16) includes 0.07 wt% CoO, 0.03 wt% NiO and 0.02 wt% ZnO, Mazdab (2001); (17) new analytical data provided for this study; includes 0.42 wt% SrO, 0.05 wt% BaO, 0.03 wt% V_2O_3 and 0.02 wt% ZrO_2.

TABLE 3. NORMALIZATION ROUTINES USED

routine name	summary	basis of normalization*
amphibole 1 [8Si]	$\Sigma(T) = 8$ (no Al, Ga in T)	$\Sigma(B+Be+Si+P+S+Ge) = 8$
amphibole 2 [8SiAl]	$\Sigma(T) = 8$ (all Al, Ga in T)	$\Sigma(B+Be+Si+P+S+Ge+Al+Ga) = 8$
amphibole 3 [13eCNK]	$\Sigma(T+[M1,M2,M3]) = 13$ (no Fe, Mg, Mn, *etc.* in $M4$)	$\Sigma(B+Be+Mg+Al+Si+P+S+Sc+Ti+V+Cr+Mn+Fe+Co+Ni+Cu+Zn+Ga+Ge+Zr+Nb+Sn) = 13$
amphibole 4 [15eNK]	$\Sigma(T+[M1,M2,M3]+M4) = 15$ (all Na in A; no Na in $M4$)	$\Sigma(B+Be+Mg+Al+Si+P+S+Sc+Ti+V+Cr+Mn+Fe+Co+Ni+Cu+Zn+Ga+Ge+Zr+Nb+Sn+Li+Ca+Sr+Y+REE) = 15$
amphibole 5 [15eK]	$\Sigma(T+[M1,M2,M3]+M4) = 15$ (all Na in $M4$; no Na in A)	$\Sigma(B+Be+Mg+Al+Si+P+S+Sc+Ti+V+Cr+Mn+Fe+Co+Ni+Cu+Zn+Ga+Ge+Zr+Nb+Sn+Li+Ca+Sr+Y+REE+Na) = 15$
amphibole 6 [16CAT]	Σ(all sites) = 16	$\Sigma(B+Be+Mg+Al+Si+P+S+Sc+Ti+V+Cr+Mn+Fe+Co+Ni+Cu+Zn+Ga+Ge+Zr+Nb+Sn+Li+Ca+Sr+Y+REE+Na+K+Ba+Pb) = 16$

The number of cations is expressed in atoms per formula unit (*apfu*). Samples were also normalized to $\Sigma(-)$ (23 oxygen basis) = $\Sigma(+)$ for $Fe^{3+}/\Sigma Fe$ ranging from 0.00 to 1.00 in 0.01 increments to evaluate permissible limits of $Fe^{3+}/\Sigma Fe$.

cies and for comparing compositional features derived from different routines of normalization. To discriminate normalization routines yielding less than ideal but still acceptable stoichiometries from those considered unacceptable, a slightly more permissive set of site-occupancy criteria was used: overfilling or underfilling by less than ±0.01 *apfu* at the *T* site (representing ±0.125%); ±0.03 *apfu* at the *C* site (representing ±0.6%); ±0.02 *apfu* at the *B* site (representing ±1%), and overfilling by less than 0.04 *apfu* at the *A* site (representing 4%). Those limited normalizations requiring these more permissive criteria are so identified (see Results section and Fig. 1).

In addition to the normalization protocols listed in Table 3, formulas for each amphibole selected were also calculated by charge balance based on 23 atoms of oxygen, for an incremental series of $Fe^{3+}/\Sigma Fe$ values ranging from 0 (all ferrous iron) to 1.0 (all ferric iron) in 0.01 steps. Again, only those $Fe^{3+}/\Sigma Fe$ values that yielded stoichiometries whose site-occupancies do not violate the more stringent site-occupancy constraints listed above were deemed acceptable. Unlike the previous case, however, marginal datasets resulting in no valid range of $Fe^{3+}/\Sigma Fe$ values for a given sample composition were *not* re-evaluated using the more permis-

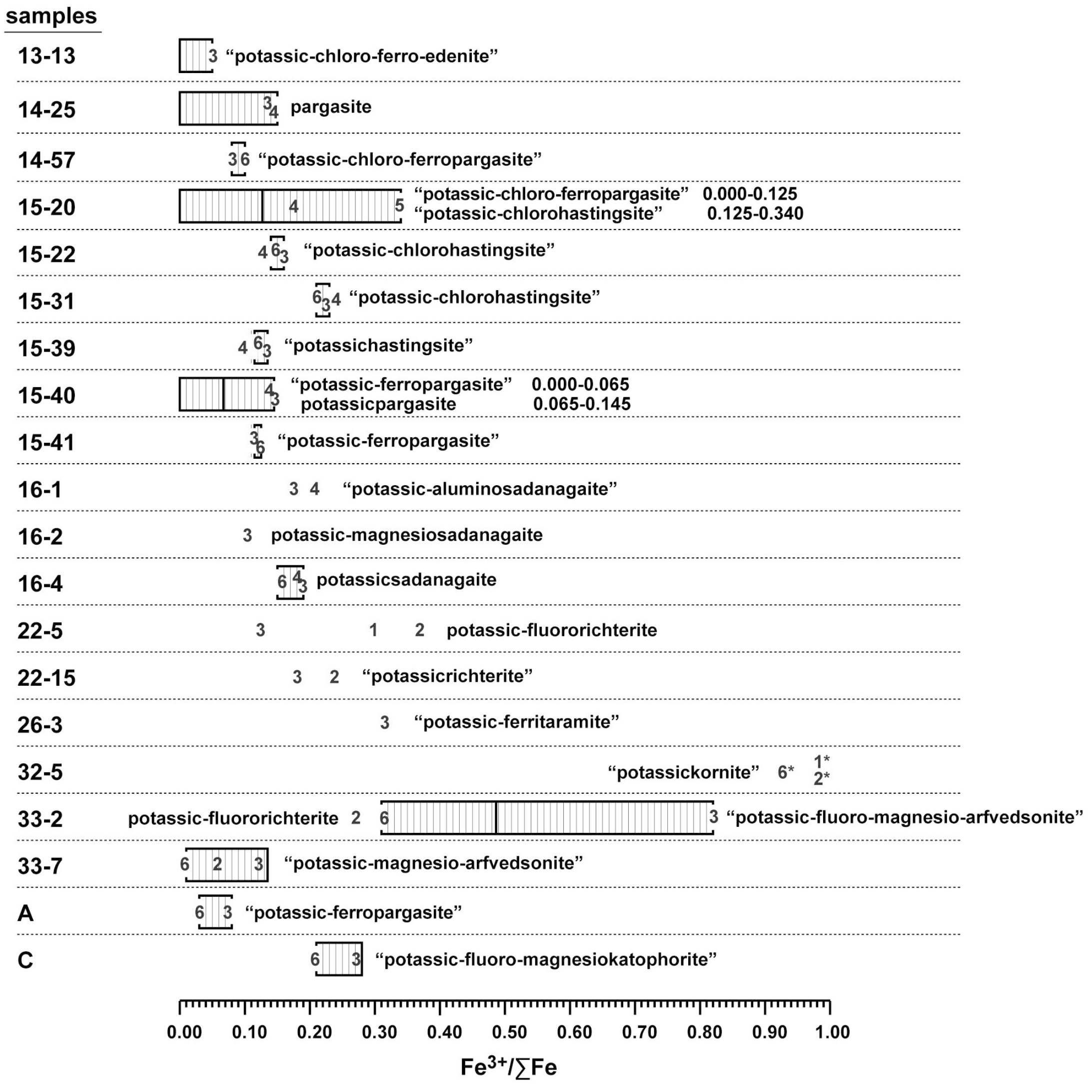

FIG. 1. Idealized ranges of Fe^{3+}/ΣFe values, stoichiometry-based limiting Fe^{3+}/ΣFe values, and derived names of amphibole species for all permissible normalization-protocols. For each sample composition, the horizontal bar indicates the idealized range of Fe^{3+}/ΣFe values that satisfy charge balance and strict site-occupancy constraints (limited to ±0.005 *apfu* variance at *T*, *C*, *B*, and *A* sites) calculated from Σ(–) (23 oxygen basis) = Σ(+) and Fe^{3+}/ΣFe = 0.00 to 1.00 stepped in 0.01 increments. For six samples (16–1, 16–2, 22–5, 22–15, 26–3, and 32–5), no value of Fe^{3+}/ΣFe satisfies the site-occupancy constraints, although deviations from ideal site-occupancy are minor only (see text), indicating that the analytical data are marginal (although still useful). The integers 1 through 6 on the diagram correspond to the positions of the limiting Fe^{3+}/ΣFe values calculated from the specific stoichiometry-based normalizations presented in Table 3; the value **1** refers to routine "amphibole 1" [8Si], **2** refers to "amphibole 2" [8SiAl], and so on. Where integers fall outside of the horizontal bar (for example, the **4** on sample 15–39), or in the absence of a bar, these normalizations calculate Fe^{3+}/ΣFe values that correspond to site occupancies slightly more permissive than the strict ±0.005 *apfu* constraint (see text for accepted limits). Three compositions (15–20, 15–40, and 33–2) show a change in the species name derived over the permissible range of Fe^{3+}/ΣFe values. The Fe^{3+}/ΣFe value where this change occurs is identified by a dark vertical line within the horizontal bar. For samples 15–20 and 15–40, owing to space limitations, both names and the corresponding numerical Fe^{3+}/ΣFe ranges for each name are given to the right of the horizontal bar. For sample 33–2, the names are located by their respective regions on the diagram and hence an explicit numerical Fe^{3+}/ΣFe range was not included. For "potassickornite" (sample 32–5), all Fe is assumed to be Fe^{3+}, and the integers identify the calculated Mn^{3+}/ΣMn values for a given normalization protocol (hence denoted with asterisks).

sive site-occupancy criteria. In this way, the idealized permissive range of $Fe^{3+}/\Sigma Fe$ values for each sample provides a consistent basis of comparison to the calculated $Fe^{3+}/\Sigma Fe$ values derived from the other normalization routines (see Fig. 1). A key underlying assumption in these calculations is that there is no significant replacement of (OH + F + Cl) by oxygen.

RESULTS

In Figure 1, I summarize, for each sample composition, the idealized valid $Fe^{3+}/\Sigma Fe$ range (determined from normalization based on charge balance), limiting $Fe^{3+}/\Sigma Fe$ values (calculated from the stoichiometry-based normalization routines listed in Table 3), and derived species names from all permissible normalization-protocols.

Most notable is the general applicability of various normalization-protocols for any given composition. Only 2 out of 20 compositions (samples 16–2 and 26–3) can be normalized by only a single normalization-protocol. In contrast, several normalizations yield acceptable results for the other 18 compositions. However, despite the applicability of multiple normalization-routines, the *range* of calculated permissible $Fe^{3+}/\Sigma Fe$ values for any given composition is generally quite small, indicating that different normalization-protocols nonetheless commonly give similar results. Indeed, for only two amphiboles (samples 15–20 and 33–2) did the range of $Fe^{3+}/\Sigma Fe$ values exceed 0.245, and typically, the range was on the order of 0.070 or less. These tight $Fe^{3+}/\Sigma Fe$ values are also reflected in the consistency of species names using different normalization-protocols, a key criterion in demonstrating an overall diversity of species. In only three of the 20 compositions do the species names change over the range of permissive normalizations: 33–2, 15–40 and 15–20. Sample 15–40 sits very near a general boundary in nomenclature ("pargasite–ferropargasite" [$Mg \approx Fe^{2+}$]) and hence is very sensitive to even slight variations in $Fe^{3+}/\Sigma Fe$. In contrast, the broad range of permissible $Fe^{3+}/\Sigma Fe$ values for samples 33–2 and 15–20 accounts for the nomenclature variability in those samples. A fourth sample very close to another general boundary, although not evident from Figure 1, is sample 33–7. In this case, the sample composition approaches the "magnesio-arfvedsonite–eckermannite" boundary [$^{VI}Al \approx Fe^{3+}$] at its lower $Fe^{3+}/\Sigma Fe$ range; however, the boundary occurs at a $Fe^{3+}/\Sigma Fe$ value (0.000) slightly below the lower permissible $Fe^{3+}/\Sigma Fe$ limit (0.011) calculated for the sample.

In all these cases, and in general where multiple names of species are possible, assignment of an accurate name requires an independent assessment of $Fe^{3+}/\Sigma Fe$. In some instances, these data are available. For Cl-rich amphiboles from the Sesia–Lanzo marbles, Italy (sample 14–57), Oberti *et al.* (1993) calculated $Fe^{3+}/\Sigma Fe$ values of 0.134 and 0.204 for two samples, derived from structure- refinement results. These data approximate the range of permissible $Fe^{3+}/\Sigma Fe$ values (0.085 to 0.125) calculated from the various normalization-protocols. In another case, the normalization routine "3" (=13eCNK; see Table 3) accurately reproduces the $Fe^{3+}/\Sigma Fe$ value and distribution in sample 33–2 as measured by wet chemistry and Mössbauer spectroscopy (Hogarth *et al.* 1987). Hogarth *et al.* (1987) reported 9.84 wt% Fe_2O_3 and 2.61 wt% FeO measured by titration, whereas normalization by protocol "3" yields 9.48 wt% Fe_2O_3 and 2.94 wt% FeO. Hogarth *et al.* (1987) also reported on the measured tetrahedral-site occupancy of iron ($^{IV}Fe^{3+}/\Sigma Fe$), with $^{IV}Fe^{3+}/\Sigma Fe = 0.085$ by Mössbauer and $^{IV}Fe^{3+}/\Sigma Fe = 0.081$ by wet chemistry. Normalization by protocol "3" yields $^{IV}Fe^{3+}/\Sigma Fe = 0.074$. Hence, sample 33–2 can be definitively named as potassic-fluoro-magnesio-arfvedsonite.

Although the assignment of a species name is unambiguous for 18 of the 20 compositions owing to the consistency of species names, irrespective of normalization protocol, there is still a range of valid normalized formulas that can be calculated. Schumacher (1997) recommended selecting a normalization factor that yields an average of the maximum and minimum $Fe^{3+}/\Sigma Fe$ estimates. Although certainly adequate, there is no chemical justification to indicate that an average value of $Fe^{3+}/\Sigma Fe$ represents the best estimate. Thus, for the recommended normalized formulas presented in Table 4, normalizations are based on the appropriate permissible $Fe^{3+}/\Sigma Fe$ values that bring the analytical totals closest to 100.00 wt%. In many cases, the difference between the maximum and minimum $Fe^{3+}/\Sigma Fe$ estimates is too small to have any major effect on the analytical total; in a few cases, however, a specific $Fe^{3+}/\Sigma Fe$ value yielding an idealized total of 100.00 wt% can be determined. The two compositions that could not be unambiguously named were treated similarly; however, alternatively using normalization protocols yielding the average permissible $Fe^{3+}/\Sigma Fe$ estimates, as recommended by Schumacher (1997), did not otherwise have an effect on the choice of species names.

DISCUSSION

Speciation and nomenclature: justification for the recognition of new potassium-dominant amphibole species

Before a mineral and its name can be accepted into the literature, they must be approved by the CNMMN (Nickel & Grice 1998). Even for the amphiboles, where a well-defined nomenclature system is now in place, analytical data supporting a new prefix–root name combination (hence species name) in the classification scheme still requires formal submission to the CNMMN (Mandarino 1998). It is notable, however, that potassium-rich amphiboles have long been identified in nature [*e.g.*, the "dashkesanite" of Krutov (1936), now potassic-chlorohastingsite]. Nonetheless, and in spite of

TABLE 4. RECOMMENDED NORMALIZATIONS OF K-DOMINANT AMPHIBOLES

DHZ	13-33	14-25	14-57	15-20	15-22	15-31	15-39	15-40	15-41	16-1
Si *apfu*	6.67	6.06	6.13	5.75	6.12	5.72	6.05	6.02	5.67	4.61
^{IV}Al	1.33	1.94	1.87	2.25	1.85	2.28	1.95	1.98	2.33	3.39
$\Sigma(T)$	8.00	8.00	8.00	8.00	8.00(c)	8.00	8.00	8.00	8.00	8.00
^{VI}Al	0.15	0.78	0.54	0.33	0.19	0.02	0.35	0.60	0.62	1.08
Fe^{3+}	0.22		0.38	1.23	0.60	1.04	0.41	0.19	0.29	0.34
Fe^{2+}	4.29	1.07	3.47	2.29	3.20	3.34	3.84	2.01	2.03	1.60
Mg	0.14	3.06	0.55	0.96	0.92	0.46	0.10	2.05	1.84	1.50
Mn^{2+}	0.19	0.00	0.03		0.06		0.22	0.02	0.02	0.01
Ti	0.01	0.09	0.03	0.17	0.04	0.13	0.08	0.12	0.19	0.46
Cr				0.02						
$\Sigma(M1,M2,M3)$	5.00	5.00	5.00	5.00	5.00	4.98	5.00	5.00	5.00	5.00
xM^{2+}		0.03 Fe 0.01 Mn		0.28 Fe			0.04 Mn	0.03 Mn		
Ca	2.00	1.96	1.91	1.53	1.96	2.00	1.96	1.97	2.00	2.00
Na			0.09	0.19	0.04					
$\Sigma(M4)$	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Na	0.18	0.40	0.22	0.01	0.37	0.24	0.49	0.28	0.06	0.30
K	0.63	0.48	0.76	0.51	0.61	0.72	0.55	0.60	0.90	0.72
$\Sigma(A)$	0.87(a)	0.93(b)	0.98	0.52	0.99	0.98(d)	1.03	0.92(e)	1.00(f)	1.03(g)
OH	0.46	1.81	0.84	0.35		0.58	1.84	1.88	1.88	2.00
F	0.18	0.07		0.51				0.10	0.11	
Cl	1.37	0.11	1.16	1.14	2.08	1.42	0.16	0.03	0.01	
optimized $Fe^{3+}/\Sigma Fe$	0.048	0.000	0.099	0.324	0.158	0.238	0.096	0.088	0.124	0.175
name*	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)

a substantial literature characterizing potassium-rich amphiboles, a limited number of potassium-dominant amphiboles have only recently (since 1997) been conferred species status. This represents an unfortunate and surprisingly enigmatic situation, especially in light of the number of otherwise "grandfathered" minerals [1784 "grandfathered" species relative to 1466 approved species as of 1990; Nickel & Nichols (1991)]. Presumably, the reluctance to confer species status to potassium-dominant amphiboles prior to the redefinition of amphibole nomenclature in 1997 was based on a perception that the potassium-dominant amphiboles should be considered to be simply potassium-rich variants of sodium-dominant amphiboles species already recognized. Indeed, in a comment on the chemical composition of the then newly discovered kornite, Armbruster *et al.* (1993) quoted a personal communication from Bernard Leake: "It is not emphasized that K > Na on the *A* position of kornite, because it would logically loom with an enormous increase in names for the amphiboles." Ironically, kornite with sodium dominant in the *A* site has not been found in nature, yet the original approved formula for kornite was given as $(Na,K)Na_2(Mg_2Mn^{3+}{}_2Li)Si_8O_{22}(OH)_2$. Recent literature is unclear as to what the current approved formula for kornite actually is; Leake *et al.* (2003) indicates the *A* site as (Na,K), whereas the CNMMN list of approved minerals gives it as (K,Na) (Nickel & Nichols 2002). Matsubara *et al.* (2002) observed: "It should be remarked that kornite has a higher K content (0.64 *apfu*) than potassicleakeite. This suggests that the name be changed to potassickornite according to the nomenclature of amphiboles (Leake *et al.* 1997)." As it is customary in the case of amphiboles with $^{A}(Na + K) \geq 0.50$ that root names apply to the Na-derivative species (B.E. Leake, pers. commun.), amphiboles with $K \geq 0.50$ should have the prefix *potassic* to draw attention to that fact. Hence, in agreement with Matsubara *et al.* (2002), I suggest that kornite, as defined by $NaNa_2(Mg_2Mn^{3+}{}_2Li)Si_8O_{22}(OH)_2$, be relegated to a hypothetical end-member, and "potassickornite" be adopted for the original type-specimen from the Wessels mine. In another similar example, Shimazaki *et al.* (1984) commented on the then newly discovered sadanagaite and magnesiosadanagaite: "Because the significance of the K/Na ratio in the amphibole structure has not yet been established, the large K/Na value should not be included in the definition of sadanagaite." Thus, as with kornite, the original formulas for sadanagaite and magnesiosadanagaite did not correspond to the chemical compositions of the type materials; however, this inconsistency was partially addressed by Mandarino (1998). Ultimately, sadana-

TABLE 4 (continued). RECOMMENDED NORMALIZATIONS OF K-DOMINANT AMPHIBOLES

DHZ	16-2	16-4	22-5	22-15	26-3	32-5	33-2	33-7	A	C
Si *apfu*	4.97	5.24	8.01	7.54	6.23	8.00	7.84	7.94	6.25	7.34
^{IV}Al	3.03	2.76		0.46	1.77		0.03	0.04	1.75	0.36
$\Sigma(T)$	8.00	8.00	8.01	8.00	8.00	8.00	8.00(n)	8.00(o)	8.00	8.00(r)
^{VI}Al	0.99	0.87		0.01	0.20				0.46	
Fe^{3+}	0.18	0.43	0.05	0.38	1.30	0.53	0.99	0.17	0.35	0.33
Fe^{2+}	1.60	1.89	0.35	1.42	2.83		0.25	1.40	3.62	1.22
Mg	1.85	1.49	4.50	2.92	0.30	2.13	3.72	3.01	0.49	3.39
Mn^{2+}	0.01	0.07	0.02	0.09	0.26	0.03	0.01	0.04	0.04	0.04
Ti	0.37	0.25	0.05	0.14	0.12		0.02	0.38	0.01	0.01
Cr							0.01			
$\Sigma(M1,M2,M3)$	5.00	5.00	4.99(i)	4.99(j)	5.00	5.00(k)	5.00	5.00	4.98(p)	5.00
xM^{2+}										0.03 Mn
Ca	2.00	1.99	0.84	0.78	1.00		0.36	0.19	2.00	0.93
Na		0.01	1.16	1.22	1.00	1.78	1.63	1.81		1.01
$\Sigma(M4)$	2.00	2.00	2.00	2.00	2.00	2.00(l)	2.00	2.00	2.00	2.00(s)
Na	0.21	0.36	0.30	0.44	0.48	0.32	0.13	0.22	0.36	0.41
K	0.75	0.62	0.67	0.59	0.56	0.65	0.63	0.72	0.56	0.58
$\Sigma(A)$	1.04(h)	0.98	0.97	1.03	1.04	0.97	0.76	0.94	0.94(q)	1.00
OH	2.00	2.00	0.80	1.31	1.81	2.00	0.95	2.00	1.34	0.75
F			1.20	0.69	0.15		1.05			1.25
Cl					0.04				0.66	
optimized $Fe^{3+}/\Sigma Fe$	0.100	0.186	0.123	0.209	0.314	(m)	0.816	0.121	0.089	0.214
name*	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)

DHZ: reference in Deer *et al.* (1997). xM^{2+} is excess Fe, Mn, or Mg at the *B* site. Additional elements in normalizations: a) includes Ca 0.06 *apfu*; b) includes Ca 0.05 *apfu*; c) includes P 0.01 *apfu* and S 0.01 *apfu*; d) includes Ca 0.02 *apfu*; e) includes Ca 0.03 *apfu*; f) includes Ca 0.04 *apfu*; g) includes Ca 0.01 *apfu*; h) includes Ca 0.08 *apfu*; i) includes V 0.02 *apfu*; j) includes V 0.02 *apfu*; k) includes Mn^{3+} 1.40 *apfu* and Li 0.91 *apfu*; l) includes Li 0.22 *apfu*; m) all Fe as Fe^{3+}; calculated $Mn^{3+}/\Sigma Mn = 0.982$; n) includes Fe^{3+} 0.13 *apfu*; o) includes Fe^{3+} 0.02 *apfu*; p) includes Co 0.01 *apfu*; q) includes Ca 0.02 *apfu*; r) includes Ti 0.30 *apfu*; s) includes Sr 0.04 *apfu*. * Name, including all modifiers: (1) "potassic-chloro-ferro-edenite"; (2) potassian pargasite; (3) "potassic-chloro-ferropargasite"; (4) fluorian potassic-chlorohastingsite; (5) potassic-chlorohastingsite; (6) potassic-chlorohastingsite; (7) manganoan "potassichastingsite"; (8) potassicpargasite; (9) "potassic-ferropargasite"; (10) titanian "potassic-aluminosadanagaite"; (11) titanian potassic-magnesiosadanagaite; (12) potassicsadanagaite; (13) potassic-fluororichterite; (14) fluorian "potassicrichterite"; (15) manganoan "potassic-ferritaramite"; (16) "potassickornite"; (17) "potassic-fluoro-magnesio-arfvedsonite"; (18) titanian "potassic-magnesio-arfvedsonite"; (19) chlorian "potassic-ferropargasite"; (20) titanian "potassic-fluoro-magnesiokatophorite".

gaite became a hypothetical end-member, and the Japanese type-materials were relisted as potassicsadanagaite and potassic-magnesiosadanagaite. However, unresolved difficulties with the chemistry and formal definitions of sadanagaite (*sensu lato*) still exist; these issues are discussed in Mandarino (1998) and Sokolova *et al.* (2001). The confusion that can arise from these discrepancies indicates a timely need for publication of an accurate and complete list of the names and formulas of all approved amphibole end-members.

The substantive history of potassium-rich amphiboles in the older literature, coupled with the former inconsistencies in nomenclature, lead to another ambiguous feature in the speciation of the potassium-dominant amphiboles: the relevance of older descriptions. For example, Nickel & Nichols (1991) listed only one potassium-dominant amphibole as of May, 1990: "potassium pargasite", which they denoted as a questionable species. The mineral, from Antarctica, had been described by Matsubara & Motoyoshi (1985), who based their conclusions on chemical compositions (including wet chemistry for H_2O and Fe_2O_3), physical and optical determinations, powder X-ray data, and paragenetic relationships. In Mandarino (1999), four potassium-dominant amphibole species are identified, all officially recognized after implementation of the Leake *et al.* (1997) protocol. One of these is the "formal description" of potassicpargasite from an unknown locality, presumably Pargas, Finland (Robinson *et al.* 1997). Although acknowledged by Robinson *et al.* (1997), Matsubara & Motoyoshi (1985) clearly fully described the mineral from Antarctica twelve years earlier. However, at that time, there was no recognition that this mineral represented a new amphibole species, but simply that is was the most potassium-rich amphibole (pargasite) so far discovered. The questionable species status of unusual end-member compositions may have had its basis in the Leake (1978) scheme of nomenclature. Leake (1978) noted in reference to prefixes: "Provision is made to denote by prefixes the presence of substantial substitution by elements that are not essential constituents of the end-members." Hence, potassium-dominant amphiboles were not afforded end-member status at the time. Similarly, with respect to suggested usage, no distinction was made between the prefixes "potassium" (= 0.50 K *apfu* at the *A* site) and "potassian" (between 0.25 and 0.49 K *apfu*) in the 1978 report (*i.e.*, neither being explicitly stated as obligatory). In contrast, in Leake *et al.* (1997), "potassic-" becomes an integral part of the end-member name, whereas "potassian" is relegated to an optional modifier. Indeed, the formal distinction between prefixes and modifiers is one of the major accomplishments of the 1997 report, providing the necessary support for the recognition of unusual end-member compositions.

Although the potassium-dominant amphiboles are starting to be officially recognized, the necessity of strict formality in conferring species status to those already historically described minerals is potentially limiting the broader use of the nomenclature protocol of Leake *et al.* (1997). Among mineral groups with well-developed compositionally derived nomenclature, the amphiboles represent some of the most widespread, chemically diverse, and geologically important minerals. Hence, the Leake *et al.* (1997) protocol could be of widespread applicability in many areas of geology not otherwise specifically concerned with amphibole mineralogy. In these situations in particular, compositional clues contained within mineral names provide immediate chemical information not only about the mineral itself, but also about compositional parameters indicative of the overall mineral assemblage or geochemical environment. Although such instant chemical recognition may seem trivial to mineralogists familiar with many formulas, the average geologist benefits the most from descriptive and systematic nomenclature. For example, in researching the mineralogy of a magnetite "skarn", a casual perusal of the literature may not warrant the attachment of much genetic significance to the occurrence of hastingsite and apatite among the list of minerals. If instead, however, the listing more accurately identified the species as "potassic-chlorohastingsite" and chloroapatite, even a geologist without an extensive mineralogy background could immediately recognize possible evidence for potassium metasomatism and for the potential involvement of high-salinity brines in the formation of this occurrence (see below). For this reason in particular, the recognition of the potassium-dominant amphiboles is a timely issue.

Certainly, with the recognition of a new mineral species comes the responsibility for accurate physical, chemical, and structural characterization, as well as deposition of type material in a national museum. These important procedures are in place to ensure the integrity of mineralogy as a science and should not be circumvented. However, for many of the examples provided in this text, these data are already present in the literature. Although it would be advantageous for the researchers who originally described these samples to submit new formal proposals to the CNMMN, that may not come to pass, particularly for those samples described decades ago that may now be lost. However, the impact of such earlier work should certainly not be diminished because of a formality. In the case of "potassic-fluoro-magnesio-katophorite" (sample C), newly identified during this study, a formal proposal to the CNMMN will be submitted once basic data on crystallographic, optical, and physical properties are collected.

Geochemical diversity and geology of potassium-dominant amphiboles

Table 1 illustrates that occurrences of potassium-dominant amphiboles include a variety of igneous, metamorphic, and hydrothermal environments. In addition, the "potassic-" amphiboles also span a broad range of bulk amphibole compositions, covering not only the extent of observed $^{IV}Al/(^{IV}Al + Si)$ values among the calcic, sodic-calcic, and sodic amphibole subgroups (= "root names"), but also the prevalent homovalent (Mg for Fe^{2+}, Al for Fe^{3+}, and F and Cl for OH) substitutions (= "prefixes"). Indeed, representative potassium-dominant compositions come from all major groups of amphibole where, by definition, $(^{A}Na + K) \geq 0.50$ *apfu* [with the possible exception of kaersutite, although the composition of the "Kakanui hornblende" widely distributed as an electron-microprobe standard (Jarosewich *et al.* 1979) normalizes to a potassian kaersutite ($K \approx 0.38$ to 0.40 *apfu*; Mazdab, unpubl. data]. Thus, although potassium-dominant equivalents of many of the sodium-dominant amphiboles may eventually be discovered, the current more-limited species diversity of the "potassic-" amphiboles suggests that the physicochemical conditions necessary for the formation of potassium-rich amphiboles are more specialized than those which give rise to the more common sodium-bearing species. Amphiboles in general, owing to their widespread occurrences and the large number of potential cation and anion substitutions possible, may thus be ideal tracers of the conditions prevalent during their formation, notwithstanding the effects of crystal-chemical controls.

The occurrences of potassium-rich amphibole represented in Table 1 may be broadly classified into three main groupings based on the dominant processes related to their formation: (1) those associated with alkali–chloride metasomatism, (2) those derived from locally K-rich *in situ* isochemical metamorphism, and (3) occurrences associated with K-rich igneous rocks and affiliated metasomatism. In addition to these three main categories, more limited examples of "potassic-" amphibole also occur in other, miscellaneous environments [*e.g.*, the metamorphosed manganiferous exhalite hosting "potassickornite" in the Wessels mine (sample 32–5); see above]. Among the groups, potassium-dominant amphiboles exhibit some notable compositional dissimilarities in both major- and minor-element make-up.

Potassium-rich amphiboles associated with alkali–chloride metasomatism

Alkali–chloride metasomatism results from the fluxing of hypersaline brines through susceptible rocks, and is commonly manifested on a large scale by regional formation of scapolite and albite (Barton & Johnson 2000). In addition to a generally distinctive suite of chlorine-rich silicate minerals including marialite, Cl-enriched amphiboles and biotite, and increasingly recognized ferropyrosmalite (Dong & Pollard 1997, Mazdab & Barton 2001), alkali–chloride metasomatism is also characteristically accompanied by spatially associated (and indeed presumably related) occurrences of iron oxide, lead–zinc, rare-earth-element (REE) – uranium, and Cu–Au–(Co–As) mineralization (for example, in the Cloncurry district of Australia, where all of these styles of mineralization occur within a widespread region of scapolite development; Williams 1998). Despite substantial economic and research interest, a full understanding of the general sources of the hydrothermal fluids and the role of associated igneous rocks at many localities remains unresolved and controversial, with advocates for both magma-derived fluids and externally sourced (perhaps in many cases evaporite-derived) brines (Barton & Johnson 1996, 2000, Hitzman *et al.* 1992, Mark & Foster 2000).

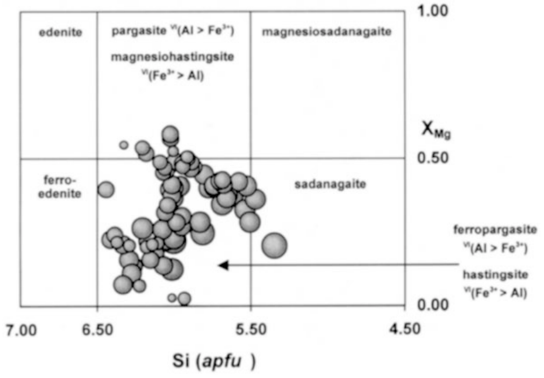

FIG. 2. The compositional range of potassian and "potassic-" calcic amphiboles associated with regional or localized alkali–chloride metasomatism. Bubble size is indicative of relative chlorine contents. X_{Mg} = Mg/(Mg + Fe^{2+}), derived from the contents of the *B* and *C* sites. Data compiled from Deer *et al.* (1997), with additional compositions taken from Dick & Robinson (1979), Enami *et al.* (1992), Gulyaeva *et al.* (1986), Jiang *et al.* (1994), Kamineni *et al.* (1982), Kullerud (1996), Kullerud & Erambert (1999), Makino *et al.* (1993), Matsubara & Motoyoshi (1985), Mazdab (2001), Mazdab & Barton (2001), Morrison (1991), Oen & Lustenhouwer (1992), Sato *et al.* (1997), Shiraishi *et al.* (1994) and Suwa *et al.* (1987).

Samples A, 13–33, 14–57, 15–22, 15–31 and 22–5 are representative of diverse lithologies affected by alkali–chloride metasomatism, irrespective of fluid source. Additional occurrences of potassium-rich amphiboles related to alkali–chloride metasomatism are summarized in Table 5. Despite substantial differences in the nature of the occurrences (with "potassic-" amphiboles developed in marble, mafic intrusive rocks, magnetite ore, and calc-silicate rock, for example), the prevalent compositions of amphibole among all of the localities are remarkably similar. With one exception, amphiboles from all of the examples are members of the calcic subgroup; the one exception is sample 22–5 from the Bufa del Diente aureole in Mexico, where local hypersaline fluids of magmatic origin are presumed to have reacted with contact-metamorphic diopside to produce potassic-fluororichterite (Heinrich 1994). The calcic amphiboles from these occurrences are further characterized by typically Fe-rich and moderately high ^{IV}Al contents, and thus are predominantly ferropargasite and hastingsite (both *sensu lato*). In addition to these bulk-composition characteristics, perhaps the most notable chemical feature of amphiboles formed by alkali–chloride metasomatism is the significant chlorine enrichment in all of the samples. Indeed, examples with over 2.0 wt% Cl are not unusual, although extremely chlorine-enriched examples comparable to the potassic-chlorohastingsite (7.24 wt% Cl, equivalent to over 2.00 Cl *apfu*) from the Dashkesan magnetite deposit in Azerbaijan (see sample 15–22) have so far not been identified from these other localities. The prevalence of "chlorian" and "chloro-" among the entries in Table 5 illustrates the nearly ubiquitous occurrence of chlorine-rich "potassic-"amphiboles associated with alkali–chloride metasomatism. The relationship between chlorine contents and bulk-amphibole composition for the potassium-rich calcic amphiboles is illustrated in Figure 2. There is a slight tendency for Cl content to increase with increasing ^{IV}Al and total Fe, comparable to trends observed by others (Makino *et al.* 1993, Morrison 1991, Oberti *et al.* 1993, Volfinger *et al.* 1985).

Potassium-rich amphiboles in metacarbonates

The transitional nature between metasomatic and predominately isochemical metamorphic origins for some potassium-rich calcic amphiboles is demonstrated by their occurrence in various marbles and calc-silicate rocks. Examples from Table 1 include samples 14–25,

TABLE 5. ADDITIONAL REPRESENTATIVE OCCURRENCES OF K-DOMINANT AMPHIBOLE ASSOCIATED WITH ALKALI–CHLORIDE METASOMATISM

representative occurrences and localities	nature of K-rich amphiboles present	reference to amphibole composition
massive pyrrhotite – chalcopyrite – magnetite ore, Osborne, Queensland, Australia	scandian chlorian hastingsite to scandian chlorian potassian hastingsite (0.06 to 0.34 Sc *apfu*; up to 2.44 wt% Sc_2O_3)	Mazdab (2001), Mazdab & Barton (2001, in prep.)
replacing vanadian clinopyroxene, altered gabbro pegmatite, Cornwall, Pennsylvania, U.S.A.	mildly V-enriched (0.02 to 0.09 V *apfu*) "potassichastingsite" to chlorian "potassichastingsite"	Mazdab (2001), Mazdab & Barton (2001)
"iron skarns", Primorye region, Far East Russia	mildly Zn-enriched (up to 0.04 Zn *apfu*) "potassichastingsite", "potassic-ferropargasite" and chlorian "potassichastingsite"	Gulyaeva *et al.* (1986)
greenschist-facies scapolite – biotite rock, Tongmugou Pb–Zn deposit, Qinling, China	potassian "chlorohastingsite" to potassic-chlorohastingsite	Jiang *et al.* (1994)
replacing plagioclase, shear zone in gabbro-anorthosite, Flakstadøy Basic Complex, Lofoten, Norway	potassian chlorian ferropargasite, potassian chlorian hastingsite, potassian "chlorosadanagaite"* and "potassic-chlorosadanagaite"*	Kullerud & Erambert (1999)
calcareous pegmatite, Lützow – Holm Bay area, Antarctica	chlorian "potassichastingsite"	Suwa *et al.* (1987)

* "chlorosadanagaite" and "potassic-chlorosadanagaite" are two new amphibole end-members not represented by any examples compiled in Deer *et al.* (1997). They are presented here as new species.

15–40, 15–41, 16–1, 16–2 and 16–4. Several of these occurrences overlap in paragenesis to some degree with the carbonate-hosted metasomatic samples described in the previous section. For example, "potassic-chloro-ferropargasite" from the Sesia–Lanzo marbles of the Italian Alps (sample 14–57) is inferred to have developed from retrograde reaction of clinopyroxene with K–Cl-rich fluids (Castelli 1988), whereas in contrast, potassian pargasite (sample 14–25) from the Tiree marble in Scotland is likely the product of nearly isochemical reaction between dolomite and either clots of feldspathic detritus or possibly "alkaline sediment" (Hallimond 1947). Although Hallimond (1947) did not elaborate on the possible nature of "alkaline sediment" at Tiree and other localities, it is interesting to speculate that in some cases, the occurrence of potassium-rich pargasite in marble can be attributable to moderate prograde metamorphism of glauconitic dolomite. A representative reaction could be:

$$\begin{aligned}&\underset{\text{“glauconite–illite”}}{2\mathrm{K}_{0.8}(\mathrm{Al}_{1.33}\mathrm{Fe}^{2+}_{0.67})[\mathrm{Al}_{0.13}\mathrm{Si}_{3.87}]\mathrm{O}_{10}(\mathrm{OH})_2}\\ &+ \underset{\text{dolomite}}{2.72\mathrm{CaMg}(\mathrm{CO}_3)_2} =\\ &\underset{\text{potassicpargasite}}{\mathrm{KCa}_2(\mathrm{Mg}_{2.72}\mathrm{Fe}^{2+}_{1.34}\mathrm{Al}_{0.94})[\mathrm{Si}_{6.02}\mathrm{Al}_{1.98}]\mathrm{O}_{22}(\mathrm{OH})_2}\\ &+ \underset{\text{calcite}}{0.72\mathrm{CaCO}_3} + \underset{\text{quartz}}{1.72\mathrm{SiO}_2} + 4.72\mathrm{CO}_2 + \mathrm{H}_2\mathrm{O}\\ &+ 0.3\text{“}\mathrm{K}_2\mathrm{O}\text{”}\end{aligned}$$

Given the widespread nature of glauconitic dolomite in modern carbonate settings, reactions of this general type might well represent an important but perhaps overlooked potassicpargasite-forming reaction during the metamorphism of impure carbonates. However, I am unaware of either experimental or field studies examining the metamorphism of glauconite beyond low-grade conversion to mica. Potassicpargasite-forming reactions can also be written with trioctahedral mica and quartz as reactants, providing an alternative mechanism for the occurrence of potassicpargasite in marbles:

$$\begin{aligned}&\underset{\text{eastonite}}{\mathrm{K}(\mathrm{Mg}_2\mathrm{Al})[\mathrm{Al}_2\mathrm{Si}_2]\mathrm{O}_{10}(\mathrm{OH})_2} + \underset{\text{dolomite}}{2\mathrm{CaMg}(\mathrm{CO}_3)_2}\\ &+ \underset{\text{quartz}}{4\mathrm{SiO}_2} = \underset{\text{potassicpargasite}}{\mathrm{KCa}_2(\mathrm{Mg}_4\mathrm{Al})[\mathrm{Si}_6\mathrm{Al}_2]\mathrm{O}_{22}(\mathrm{OH})_2} + 4\mathrm{CO}_2\end{aligned}$$

Maamar *et al.* (1992), as reported in Deer *et al.* (1997), examined a variant of this reaction: preiswerkite + 2 diopside = pargasite, under hydrothermal conditions

TABLE 6. ADDITIONAL REPRESENTATIVE OCCURRENCES OF K-DOMINANT AMPHIBOLE ASSOCIATED WITH IGNEOUS ROCKS AND RELATED METASOMATISM

representative occurrences and localities	nature of K-rich amphiboles present	reference to amphibole composition
syenite; Moradungri, Barado District, India	titanian potassicpargasite	Sadashivaiah & Durgadmath (1974) (as reported in Deer *et al.* 1997)
megacrysts in volcanic breccia, Kakanui, New Zealand	titanian potassian pargasite to potassian kaersutite	Mason & Allen (1973); also Mazdab (unpublished data)
diamond-bearing micaceous kimberlite, Sover North mine, Cape Province, South Africa	titanian "potassicrichterite"	Mitchell (1995)
lamproite, West Kimberley, Australia	titanian potassic-fluororichterite	Oberti *et al.* (1992)
phlogopite pyroxenite nodule, kimberlite, Wesselton, South Africa	relatively low Ti (0.06 Ti *apfu*) potassicrichterite	Erlank & Finger (1970)
nepheline syenite and associated fenites, Darkainle nepheline syenite complex, Somalia	"potassic-ferritaramite"	Brock *et al.* (1964)
lamproite, Napoleon Bay, Baffin Island, Canada	"potassic-titano-arfvedsonite"*, "potassic-ferrorichterite"*, "potassic-titano-magnesio-arfvedsonite"* (possibly "potassic-titano-ferric-ferronyöbite"*)	Hogarth (1997)

* Note that "potassic-titano-arfvedsonite", "potassic-ferrorichterite", "potassic-magnesio-arfvedsonite" and "potassic-titano-ferric-ferronyöbite" nominally indicate four new species of amphibole not represented by any of the analyzes samples compiled by Deer *et al.* (1997). However, only two of the four compositions presented by Hogarth (1997) can be normalized using the criteria used herein; other assumptions may be necessary to normalize the other compositions, including which degree of tetrahedral site-occupancy by Fe^{3+} and Ti is appropriate, and the possibility of O replacing (OH + F + Cl). The extreme Ti enrichment of these samples may also warrant new Ti-bearing end-members in the sodic amphibole subgroup, akin to kaersutite in the calcic amphibole subgroup. In any case, additional study is needed to verify the species status of these amphiboles; however, "potassic-ferrorichterite" is indeed indicated from the normalization and is presented here as a new species.

between 700 and 800°C and 1–2 kbar hydrostatic pressure. Where fluorian potassicpargasite is present, as at Pargas, Finland (see earlier discussion), the fluorine component may have a source in sedimentary carbonate-fluorapatite or fluorite.

Although potassicpargasite and fluorian potassicpargasite are the dominant potassium-rich amphibole compositions in metacarbonates, other Cl-free and generally Mg-rich compositions also may occur. For example, the "skarn" titanian "potassic-aluminosadanagaite" and titanian "potassic-magnesiosadanagaite" (samples 16–1, 16–2, and 16–4) described by Shimazaki *et al.* (1984) are also believed to be largely the result of isochemical metamorphism of intercalated limestones and Al-, Fe-, and Ti-rich sediments. Indeed, "potassicsadanagaite"-forming reactions, comparable to the listed potassicpargasite-forming reactions but involving illite or muscovite rather than glauconite or biotite, can be envisioned. However, Shimazaki *et al.* (1984) suggested the possibility of some limited involvement of localized metasomatism as well.

Potassium-rich amphiboles in igneous environments

Samples C, 15–39, 22–5, 26–3, 33–2 and 33–7 are representative of a variety of igneous environments and associated metasomatism (such as fenitization). Additional representative localities are summarized in Table 6. Unlike the relatively small chemical variability seen in potassium-rich amphiboles associated with alkali–chloride metasomatism, the magma-related potassium-rich amphiboles are significantly more diverse, and include compositions from the calcic, sodic-calcic and sodic subgroups. In addition, unlike the metasomatic amphiboles, Fe/Mg values and ^{IV}Al contents of the igneous amphiboles are also more variable and generally reflect the overall igneous bulk-composition. Hence, iron-rich, moderate to high ^{IV}Al-content amphiboles, such as calcic subgroup "potassichastingsite" or sodic-calcic subgroup "potassic-ferritaramite", might be typical of evolved peralkaline granitic and syenitic rocks, whereas in contrast, Mg-rich and Al-poor amphiboles such as sodic-calcic subgroup "potassicrichterite" and sodic subgroup "potassic-magnesio-arfvedsonite" (both *sensu lato*) would be typical of more magnesian rocks such lamproites and minettes.

Although the bulk compositions of this group are more diverse, one notable geochemical feature is the significant enrichment in Ti, evident from some of the normalizations in Table 4 and the additional localities presented in Table 6. The Ti enrichment noted in many of these samples is not unusual for igneous amphiboles in general; indeed, among all of the compositional subgroups (calcic, sodic-calcic, and sodic), elevated Ti in igneous amphiboles is the dominant minor-element difference compared to amphiboles of an alkali–chloride metasomatic origin, which tend to have little to no titanium. Anion-site make-up also is dissimilar between the igneous and alkali–chloride metasomatic amphiboles. Where reported, chlorine in igneous potassium-rich amphiboles rarely exceeds a few tenths of a weight percent, although in contrast fluorine may be abundant in the igneous amphiboles.

CONCLUSIONS

Potassium-dominant amphiboles occur in many rock types and show a rich variability in composition and paragenesis. The paragenetic significance of potassium-dominant amphiboles requires new species names derived from the existing scheme of nomenclature. This development would clarify the chemical environment represented by the amphibole and help place the petrography in context. Since species names of amphiboles may depend on the technique of normalization chosen, representative compositions analyses of potassium-rich amphiboles compiled by Deer *et al.* (1997) were re-normalized by several accepted normalization-protocols to verify their constancy of formula, a prerequisite to accurate species identification and naming. Using the current accepted scheme of nomenclature of Leake *et al.* (1997), names for these example amphiboles from Deer *et al.* (1997) and other literature sources have been updated.

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