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IMPLICATIONS OF THE PRESENCE OF AMAZONITE IN THE BROKEN HILL AND GECO METAMORPHOSED SULFIDE DEPOSITS

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ABSTRACT

Deep green amazonite from granitic pegmatites in the Broken Hill Pb–Zn–Ag deposit, Australia, and pale bluish green amazonite from granitic pegmatites in the Geco Cu–Zn deposit at Manitouwadge, Ontario, are compared. The amazonite is notably enriched in lead (Broken Hill: 1 to 2% Pb, Geco: 0.1 to 1%). The lead content is correlated with intensity of coloration, although exceptions are common. The amazonite occurs in both monoclinic (Broken Hill) and triclinic forms (Geco); the lead content appears to exert no control on degree of Al–Si order, which can mainly be attributed to the thermal history of the crustal blocks after emplacement of the pegmatites. The Pb-isotope composition of the amazonite is very similar to that of the galena from the orebodies, indicating a common source for the lead. The lead appears to have been released by desulfurization of the orebodies during metamorphism and was incorporated in anatectic granitic liquids, which probably formed *in situ* in the ore zone. The occurrence of amazonite may be used as a guide to base-metal mineralization in medium- to high-grade metamorphic terranes, although its defect structure may be annealed during cooling by interaction with a late sulfur-bearing fluid phase. Inferences may be made concerning the different thermal and uplift histories of the two crustal blocks on the basis of feldspar mineralogy.

Keywords: amazonite, lead, microcline, orthoclase, Broken Hill, Australia, Geco, Ontario, lead isotopes, degree of Al–Si order, desulfurization reaction, anatexis.

SOMMAIRE

On compare l'amazonite vert foncé de pegmatites granitiques du gisement Pb–Zn–Ag de Broken Hill, en Australie, avec l'amazonite vert bleuâtre pâle de pegmatites granitiques du gisement Cu–Zn de Geco, à Manitouwadge, en Ontario. L'amazonite est très enrichie en plomb (entre 1 et 2% Pb pour les échantillons de Broken Hill, 0.1 et 1% pour ceux de Geco). La teneur en plomb montre une corrélation avec l'intensité de la coloration, quoique les exceptions sont courantes. On trouve l'amazonite sous formes monoclinique (Broken Hill) et triclinique (Geco); la teneur en plomb ne semble pas déterminer le degré d'ordre Al–Si, qui résulterait plutôt de l'évolution thermique de blocs crustaux après la mise en place des pegmatites. La composition isotopique du plomb de l'amazonite est très semblable à celle de la galène des gisements, indication d'une source commune du plomb. Ce plomb semble avoir été libéré suite à une perte de soufre pendant le métamorphisme des gisements, et aurait été incorporé dans les liquides granitiques anatectiques formés *in situ* dans les zones minéralisées. Les indices d'amazonite peuvent servir comme guides aux zones minéralisées en métaux de base dans les socles soumis à un métamorphisme moyen ou élevé, quoique les défauts dans sa structure peuvent être éliminés pendant le refroidissement par interaction avec une phase fluide tardive porteuse de soufre. On peut utiliser la minéralogie des feldspaths pour préciser les différences dans l'évolution thermique ou le taux de soulèvement de deux blocs crustaux.

(Traduit par la Rédaction)

Mots-clés: amazonite, plomb, microcline, orthose, Broken Hill, Australie, Geco, Ontario, isotopes de plomb, degré d'ordre Al–Si, réaction de désulfurisation, anatexie.

INTRODUCTION

Amazonite is usually defined as a bluish green variety of triclinic potassium-rich feldspar (*i.e.*, microcline). The definition was extended by Čech *et al.* (1971) to include green K-rich feldspar that appears to be monoclinic in symmetry (*i.e.*, orthoclase). Data are here presented on the composition, degree of Al–Si order and lead-isotope geochemistry of amazonite and associated uncolored K-feldspar from two similar occurrences: 1) Broken Hill, Australia, and 2) the Geco mine, Manitouwadge, Ontario. In both cases, the amazonite is a constituent of granitic pegmatites emplaced near a metamorphosed base-metal orebody. Amazonite is not only a decorative curiosity; it appears to be a direct consequence of sulfide-silicate equilibria, and as such can be used as a guide to sulfide mineralization in high-grade metamorphic terranes.

BACKGROUND INFORMATION ON THE NATURE OF AMAZONITE

Amazonitic K-feldspar typically occurs in granitic pegmatites. There, it may be associated with "normal" K-feldspar; compared to the latter, it is systematically enriched in lead (*e.g.*, Zhirov & Stishov 1965, Čech *et al.* 1971, Foord & Martin 1979, Hofmeister & Rossman 1985). There are two ways to accommodate lead in the structure of K-feldspar: 1) coupled substitution of Pb^{2+} + Al^{3+} for K^{+} + Si^{4+}, the type of mechanism that accounts for the

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plagioclase series, and 2) $Pb^{2+} + \square$ for $2K^+$, leading to a defect structure, suggested by Plyusnin (1969). However, Pb^{2+} cannot cause the color, because its electronic transition lies in the ultraviolet part of the spectrum (*e.g.*, Hofmeister & Rossman 1985). Marfunin & Bershov (1970) proposed that Pb^+ centres are a more likely cause of the characteristic color. Hofmeister & Rossman (1985) used results of visible, infrared and electron paramagnetic resonance spectroscopy to show that Pb^{3+} could be the coloring ion, and that the unusual charge results from a reaction of the Pb^{2+} with products of dissociation of structurally bound water (uncharged OH and H) upon radiation.

A given sample of amazonite contains "active" lead, intimately associated with a molecule of water and causing the blue-green or green color, and "inactive" lead, which may be located too far from a molecule of water to allow the reaction to take place, or which may reside in the structure according to the scheme of substitution $Pb^{2+} + Al^{3+} = K^+ + Si^{4+}$ (Hofmeister & Rossman 1985).

The degree of Al-Si order of the K-feldspar exerts an influence on the wavelength of light absorbed. Hofmeister & Rossman (1985) found that samples with the bluest hues are invariably microcline, whereas yellowish green samples all consist of orthoclase. They also found that the bluest amazonitic microcline (their type-B amazonite) typically contains less than 0.2 weight % PbO, whereas the green orthoclase (type-G amazonite) contains more than 1% PbO, and may attain 1.8%.

GEOLOGICAL SETTING OF THE SUITES EXAMINED

Broken Hill, Australia

The Broken Hill Block, in southern Australia, consists of an apparently conformable succession of Early Proterozoic groups and formations that comprise the Willyama Supergroup (Willis *et al.* 1983). The world's largest high-grade Pb–Zn–Ag deposit occurs in the Broken Hill Group (500 - 1500 m thick), which consists of pelitic, psammopelitic and psammitic metasediments deposited approximately 1800 Ma ago (now quartz–feldspar–biotite–garnet paragneiss, K-feldspar > plagioclase), with minor felsic and basic gneissic rocks and banded iron-formation. Concordant granite gneiss occurs toward the base of the sequence. The orebodies appear to be laterally equivalent to the felsic gneisses, which may represent recrystallized felsic pyroclastic material (Willis *et al.* 1983, Plimer 1984, 1985). Some rocks associated with the orebodies have an unusual composition interpreted in terms of a mixture of clastic material and chemical precipitates (exhalites). The rocks of the Broken Hill Block are complexly folded; three major episodes of deformation have been recognized (Laing *et al.* 1978, Laing 1980). There is a general increase in metamorphic grade from northwest to southeast; the orebodies and the granitic masses occur in the high-grade terrane. The regional gradient may reflect regional tilting of the block to reveal a deeper crustal section to the southeast.

Pegmatite lenses occur throughout the district in sillimanite gneiss as well as within and between orebodies. They are unzoned (Plimer 1976) and locally deformed with the enclosing orebodies (Johnson & Klingner 1976). The pegmatites are thus syn- to post-kinematic. The so-called Separation pegmatite, located between the two lowermost stratiform orebodies of the Broken Hill deposit, consists of microperthitic to nonperthitic grey-white to green orthoclase in crystals up to 10 cm across, quartz and minor plagioclase, muscovite, garnet, galena, sphalerite, apatite and zircon. Pegmatite stringers cut through parts of the main body. Close to the orebody, the pegmatite stringers contain type-G amazonite and minor amounts of sulfides; away from the orebody, the stringers contain grey-white K-feldspar, and are free of sulfides (Plimer 1976).

The granitic pegmatites at Broken Hill are likely the product of *in situ* partial metling of quartzofeldspathic sediments during the culmination of metamorphism, which reached the upper amphibolite to granulite facies in the area (Phillips & Wall 1981, Corbett & Phillips 1981). The rocks of the Willyama Supergroup are inferred locally to have attained 800°C at a confining pressure between 5 and 6 kbar (Phillips & Wall 1981).

The generally accepted age of high-grade metamorphism of the Willyama Complex is 1660 Ma (Stacey & Kramers 1975). Shaw (1968) obtained a Rb/Sr age of 1660 ± 10 Ma for rocks of the Mine Sequence, and Reynolds (1971) determined an age of 1660 ± 16 Ma from a $^{206}Pb/^{204}Pb$ *versus* $^{207}Pb/^{204}Pb$ whole-rock isochron. Gulson (1984) derived U–Pb dates of 1565 ± 20 Ma for apatite from rocks of the Lode Horizon and Mine Sequence, 1595 Ma for monazite and titanite, and 1663 ± 9 Ma for zircon from granitic gneiss underlying the Broken Hill Group.The 1565 and 1595 Ma dates are interpreted to be cooling ages. The orebody and enclosing rocks probably remained above the blocking temperature of apatite (taken to be approximately 600°C) for 60 or 70 Ma (Gulson 1984). The area cooled slowly (approximately $3°C\ Ma^{-1}$) until about 1570 Ma ago, when the temperature fell below about 500°C (Harrison & McDougall 1981); the $^{40}Ar/^{39}Ar$ age spectra also indicate that the region remained relatively cold until affected by a thermal pulse 520 ± 40 Ma ago. This caused temperatures to rise locally to 350°C. The emplacement of a suite of ultramafic intrusive bodies exposed in the area ultimately may be found to be responsible for the Early Paleozoic thermal event.

The Geco mine, Manitouwadge, Ontario

The Manitouwadge area in north-central Ontario is host to the Geco massive Cu–Zn sulfide deposit (Friesen *et al.* 1982). The deposit is located in the Manitouwadge pegmatite series, which straddles the contact between the metamorphosed strata of the greenstone belt and the surrounding Archean basement. The pegmatites abut against the orebody, and in this specific environment, specimens of amazonite may be found.

The Manitouwadge greenstone belt is composed of metamorphosed volcanic and sedimentary rocks that have undergone at least two phases of folding to produce an east-northeast-plunging synform (Bakker *et al.* 1985). The strata have been metamorphosed to the upper amphibolite facies (James *et al.* 1978) or lower granulite facies (Petersen & Friesen 1982) during the Kenoran orogeny. The core of the synform and the country rocks are composed of granitic and granodioritic gneisses, with patches of massive granodiorite and associated pegmatites. Late-stage granodiorite, pegmatites and diabase dykes cross-cut the synform. A lack of deformation features indicates that they were emplaced after the second episode of deformation.

The pegmatites are likely the product of anatexis. Metamorphic conditions at Manitouwadge were certainly conducive to melting. James *et al.* (1978) determined the maximum pressure and temperature of metamorphism to have been in the range 3 to 6 kbar [$P(H_2O) < P_{total}$] and 625°C using the garnet - biotite - cordierite assemblage. More recently, Petersen (1983) proposed 6 kbar and 650°C on the basis of various sulfide, silicate and oxide equilibria. The presence of migmatites is consistent with the proposal that favorable conditions for anatectic reactions did prevail. The gaseous fraction trapped in cordierite in a pegmatite from the Manitouwadge area is much richer in H_2O than CO_2, and was trapped above 600°C (Aines & Rossman 1984). Robinson (1979) proposed the formation of extensive quartzofeldspathic melts by ultrametamorphism of wacke-type sedimentary rocks in the area.

The Superior Province in this area last underwent an episode of regional metamorphism during the Kenoran orogeny, some 2700 Ma ago. Extensive investigations of the radiometric age of the gneisses and ore minerals at Geco have been made by Rb/Sr and U–Th–Pb methods (Tilton & Steiger 1965, 1969, Oversby 1978). Tilton & Steiger (1969) obtained an average age of 2720 ± 50 Ma from mineral and whole-rock data. The accepted model age for Geco galena is 2700 Ma (Stacey & Kramers 1975). Ratios of the isotopes of common Pb in non-amazonitic K-feldspar from pegmatites from the Manitouwadge area vary widely (Tilton & Steiger 1969, Sinha 1969, Stacey & Kramers 1975, Oversby 1978).

The pegmatites cut all lithologies except the massive portion of the Main Orebody and younger dykes of diabase. As the ore is regarded to be syngenetic with the host lithologies, Suffel *et al.* (1971) proposed that the pegmatites do not cut the orebodies because the ore flowed plastically during the waning stages of metamorphism and sheared off the cross-cutting pegmatites. This interpretation is further supported by the occurrence of blocks of pegmatite dykes suspended in the ore (Suffel *et al.* 1971).

The amazonite is relatively common in the mine (F.J. Bakker, pers. comm., 1985); it was sampled in two pegmatite dykes (denoted 6 and 10), within 10 cm of the ore–pegmatite contact. (These dykes may consist of medium-grained granite or aplite

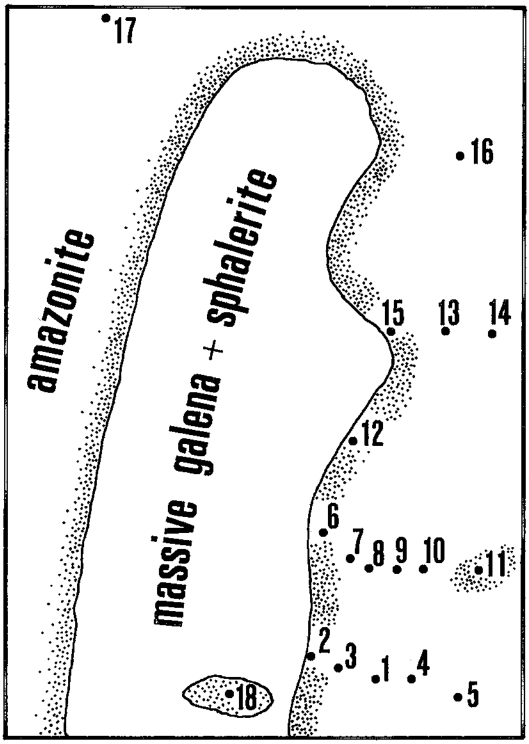

FIG. 1. Sampling sites in a coarse single crystal of amazonite and in the fine-grained retrograde assemblage (stippled) at the contact with massive galena + sphalerite; specimen E9155, Broken Hill. The retrograde zone contains white K-feldspar, albite, quartz, muscovite and very fine-grained galena. Site 18 is an inclusion of white K-feldspar. At site 11, a white halo is developed around an inclusion of galena. Loss of color in the amazonite corresponds with decreasing Pb content. Concentrations at the different sites are as follows (in ppm; see also Table 2): 1 13870, 2 1840, 3 9310, 4 14690, 5 14430, 6 230, 7 10370, 8 12840, 9 13100, 10 9350, 11 2460, 12 60, 13 13030, 14 14670, 15 640, 16 15000, 17 13760, 18 1140. Width of field of view: 2.5 cm.

rather than true pegmatite, but to be consistent with mine terminology they are all referred to as pegmatites.) Dyke 6 is located on the 21–52 sublevel of the mine. The dyke coarsens from an aplite to a medium-grained granite at the ore–pegmatite contact. The second amazonite occurrence is found in a pegmatite lens enclosed in the 8/2 zinc zone in the 28–63 stope on the 28–50 level in the mine. The lens is about 1.5 m long, 0.5 m across and unzoned; on average, grains are 8 mm across.

The grains of amazonite and white K-feldspar at Geco exhibit grid twinning typical of microcline, and are nonperthitic to microperthitic. A graphic intergrowth of quartz and K-feldspar is common both in the aplitic groundmass and in the coarser-grained portions. Discrete grains of quartz, plagioclase and muscovite comprise the rest of the rock. Sulfide veins are common in the pegmatites near the ore contact. Robinson (1979) also found that interstitial sulfides in the bodies of pegmatites occur almost exclusively near contacts with the orebody. Common sulfides include chalcopyrite, sphalerite, pyrite and pyrrhotite. Microscopic grains of galena are occasionally found in fractures in the pegmatite as well as in microfissures in the amazonite. Gahnite and garnet are also found locally.

DESCRIPTION OF THE SAMPLES SELECTED

Broken Hill

Electron-microprobe analyses were made on a gemmy sample of amazonite (E9155) from the Separation pegmatite. This sample is associated with quartz, albite, apatite, sphalerite and galena and is nonperthitic to microperthitic. Retrograde recrystallization has produced a rim of quartz, albite, muscovite and fine-grained white K-feldspar around many of the amazonite crystals (Fig. 1). Random inclusions of galena in the altered areas of the amazonite and disseminated galena in the retrograde rim are common. The color of the feldspar changes from green to white to grey or black as the galena-bearing portions are approached, as noted by Plimer (1976) and Čech *et al.* (1971). In the sample collection, the color of the amazonite varies from pale grey-green through apple green to "bottle" green; in any one sample, however, the intensity of the color is uniform.

Three additional examples of amazonite (BH4, 6 and 7) and a grey-white megacryst (BH3) from the Separation pegmatite were used for X-ray-diffraction, X-ray-fluorescence (major and minor elements) and lead-isotope studies.

Geco

The color of amazonite from the Geco mine varies (grain to grain) from pale green to apple green to a medium-dark green with a bluish tint. Not all the K-feldspar grains in a single hand-specimen are green; many are white, grey-white or pink. Electron-microprobe analyses were carried out on samples from dykes 6 and 10; X-ray-diffraction, X-ray-fluorescence and lead-isotope analyses were carried out on mineral separates 6F, 6D, 10A1 (amazonite-bearing) and 6P, 10-16 and 30-4 (white K-feldspar). Note that pegmatite samples 10-16 and 30-4 are taken from locations distal with respect to the ore zone.

ANALYTICAL TECHNIQUES

Major- and trace-element data were determined by X-ray fluorescence using a Philips PW 1400 spectrometer. Analytical precision for major elements is 1% absolute; for trace elements, it is 5% absolute. Electron-microprobe data were obtained on a Cameca Microbeam MB-1 using wavelength dispersion. The beam current was 10 nA, and counting times on samples and standards were 10 seconds for all elements except Ba (50 s) and Pb (150 s). The following standards were used: orthoclase (Si, Al, K), andradite (Fe, Ca), MgO (Mg), albite (Na), $BaSO_4$ (Ba) and vanadinite (Pb). Average levels of detection for Ba and Pb were found to be about 900 and 400 ppm, respectively. The isotopic composition of the lead in K-feldspar and galena concentrates was determined on a Micromass 30 mass spectrometer at the University of Alberta, under the supervision of Professor G.L. Cumming. Grains of galena were hand-picked and dissolved in 2N HCl overnight, and the solution evaporated to dryness. The chloride residue was washed in HCl to remove the more soluble Zn, Fe and Ag chlorides. The feldspar separates were digested overnight in a covered HF–HNO_3 mixture. The residue after evaporation was dissolved twice in concentrated HNO_3 to remove fluoride

TABLE 1. THE CHEMICAL COMPOSITION OF AMAZONITE FROM BROKEN HILL

	1	2	3	4	5	6	7	8	9
SiO_2 wt.%	63.00	63.25	64.29	63.67	64.03	66.98	63.93	62.73	64.54
Al_2O_3	18.56	18.96	19.05	19.00	18.93	17.18	19.13	18.44	18.79
FeO	-	0.06	0.06	-	0.03	0.06	0.14	0.02	0.04
MgO	-	trace	-	-	nd	nd	nd	0.07	nd
CaO	-	0.40	0.05	0.04	0.34	0.30	0.22	0.21	0.18
Na_2O	0.59	0.88	0.81	0.85	2.20	2.52	2.00	2.80	1.68
K_2O	14.94	14.95	14.43	14.75	12.23	10.28	13.07	14.65	13.94
BaO	0.04	trace	0.07	0.09	-	0.02	0.14	nd	-
PbO	1.79	1.19	1.48	1.62	1.39	1.95	1.10	1.16	0.30
total	98.92	99.69	100.24	100.02	99.15	99.29	99.73	100.08	99.47
Pb ppm	16610	11050	13760	15000	12900	18100	10210	10770	2780
Ab mole %	5.7	7.9	7.8	8.0	20.7	26.2	18.4	16.8	15.2
Or	94.3	88.1	91.7	91.6	75.8	70.4	79.3	81.2	83.0
An	-	4.0	0.5	0.4	3.5	3.4	2.3	2.0	1.8

All samples are grey-green to emerald green except number 9, which is grey-white. Total iron is expressed as FeO; nd: not determined. Composition 1 was determined by microprobe analysis by Hofmeister (1984). Composition 2 includes 0.04% SrO, 0.30% Rb_2O, 0.10% Li_2O, determined by wet-chemical analysis (Čech *et al.* (1971). Compositions 3 and 4 determined by electron microprobe, this study. Compositions 5-7, 9 determined by X-ray fluorescence, this study. Composition 8 determined by X-ray fluorescence (Plimer 1976).

TABLE 2. CHEMICAL COMPOSITION OF K-FELDSPAR IN SPECIMEN E9155, BROKEN HILL

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
SiO_2 wt.%	64.17	65.59	64.40	63.46	63.51	65.76	64.42	64.12	64.66	65.37	66.34	64.69	63.78	63.58	65.82	63.67	64.29	65.82
Al_2O_3	18.77	18.75	18.82	19.02	18.69	18.88	18.78	18.96	19.05	19.06	18.68	18.66	18.89	18.75	18.92	19.00	19.05	18.77
FeO	-	-	0.04	-	-	-	-	0.07	-	0.04	-	-	-	-	-	-	0.06	0.07
MgO	-	0.02	0.01	-	-	-	0.01	-	0.02	-	-	-	0.05	0.03	-	-	-	-
CaO	0.06	0.01	0.08	-	0.02	-	0.08	-	-	0.04	0.02	0.01	0.01	-	-	0.04	0.05	0.04
Na_2O	0.85	0.54	0.86	0.75	0.96	0.33	0.73	0.96	0.85	0.55	0.30	0.25	0.92	0.73	0.66	0.85	0.81	0.75
K_2O	14.69	15.33	14.46	14.95	15.11	16.29	13.84	14.49	14.58	14.13	14.51	17.10	15.05	15.15	15.87	14.75	14.43	15.74
BaO	0.09	0.28	0.04	0.07	0.01	0.11	0.04	0.01	0.07	0.07	0.01	0.07	0.04	0.03	0.05	0.09	0.07	0.15
PbO	0.49	0.20	1.00	1.58	1.55	0.02	1.12	1.38	1.41	1.03	0.26	0.01	1.40	1.58	0.07	1.62	1.48	0.12
total	99.12	100.72	99.71	99.83	99.85	101.39	99.02	99.99	100.64	100.29	100.12	100.79	100.14	99.85	101.39	100.02	100.24	101.46
Pb ppm	13870	1840	9310	14690	14430	230	10370	12840	13100	9350	2460	60	13030	14670	640	15000	13760	1140
Ab mole %	8.0	5.1	8.2	7.1	8.8	3.0	7.3	9.1	8.1	5.6	3.1	2.2	8.5	6.8	5.9	8.0	7.8	6.7
Or	91.4	94.8	90.9	92.9	91.0	97.0	91.8	90.9	91.9	94.0	96.7	97.7	91.4	93.2	94.1	91.6	91.7	92.9
An	0.6	0.1	0.9	-	0.2	-	0.9	-	-	0.4	0.2	0.1	0.1	-	-	0.4	0.5	0.4

Compositions determined by electron-microprobe analysis. Total iron is reported as FeO. Compositions 1 to 18 pertain to locations shown in Figure 1.

TABLE 3. CHEMICAL COMPOSITION OF AMAZONITE IN PEGMATITE FROM MANITOUWADGE

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO_2 wt.%	65.14	65.53	65.32	65.35	65.53	64.50	65.15	64.84	63.75	64.58	64.84	64.66	64.31	64.11	63.92
Al_2O_3	18.72	18.56	18.83	18.72	18.69	18.74	18.89	18.68	18.79	18.83	18.61	18.62	18.85	18.70	18.77
FeO	0.02	0.32	0.01	0.01	0.02	0.02	0.07	-	-	-	0.01	0.04	0.01	0.01	0.01
MgO	trace	-	trace	0.03	0.01	0.02	0.04	-	0.02	-	0.04	0.04	-	0.01	0.02
CaO	0.01	0.03	0.03	0.01	0.03	0.01	0.06	0.01	0.05	0.01	0.01	0.02	0.04	0.02	0.02
Na_2O	0.45	0.54	0.65	0.62	0.67	0.48	1.03	1.04	0.89	0.96	0.42	0.84	0.42	0.88	0.69
K_2O	15.48	14.85	13.78	14.06	14.91	14.89	14.83	15.37	16.03	15.13	16.50	15.50	17.06	16.17	16.35
BaO	0.13	0.65	-	0.09	0.09	trace	trace	0.04	0.02	0.14	0.01	0.05	0.26	0.25	0.09
PbO	0.60	0.49	0.56	0.20	0.33	0.36	0.69	0.39	0.64	0.40	0.48	0.72	0.37	0.62	0.37
total	100.55	100.07	99.18	99.09	100.28	98.72	100.76	100.37	100.19	100.05	100.92	100.49	101.32	100.77	100.24
Pb ppm	5570	4550	5200	1850	3060	3340	6400	3620	5940	3710	4455	6680	3435	5755	3435
Ab mole %	4.2	5.2	6.7	6.3	6.4	4.7	9.5	9.3	7.7	8.8	3.6	7.6	3.6	7.6	6.0
Or	95.7	94.5	93.0	93.6	93.3	95.2	89.9	90.6	91.8	91.1	96.3	92.2	96.0	92.2	93.8
An	0.1	0.3	0.3	0.1	0.3	0.1	0.6	0.1	0.5	0.1	0.1	0.2	0.4	0.2	0.2

Average chemical composition of amazonite from individual samples determined by electron microprobe. Samples: 6AOC (1 and 2), 6D (3 to 7), 10AO (8), 10B20 (9 to 12), R2150 (13 to 15). Total iron is expressed as FeO.

TABLE 4. COMPOSITION OF WHITE K-FELDSPAR IN PEGMATITE FROM MANITOUWADGE

	6P	2A	6AD	6AP	10AO	6D	10B20	R2150	6F
SiO_2 wt.%	64.78	65.11	64.32	64.75	64.30	65.14	64.48	63.56	64.76
Al_2O_3	18.55	18.57	18.68	18.80	18.75	18.70	18.73	18.70	18.49
FeO	0.03	0.03	0.04	0.01	0.01	0.03	0.01	0.01	0.01
MgO	0.02	0.29	0.02	trace	0.02	0.01	0.01	0.01	0.01
CaO	0.03	0.02	0.08	0.05	0.04	0.02	0.04	0.03	0.02
Na_2O	0.63	0.58	0.85	0.61	0.72	0.66	0.72	0.65	0.68
K_2O	16.21	16.33	15.67	15.86	15.93	14.74	15.76	16.26	14.83
BaO	0.07	0.03	0.10	0.07	0.07	0.09	0.07	0.39	0.11
PbO	0.08	0.11	0.62	0.32	0.42	0.36	0.55	0.46	0.53
total	100.40	101.07	100.38	100.47	100.26	99.75	100.37	100.07	99.44
Pb ppm	740	1020	5755	2970	3900	3340	5105	4270	4920
Ab mole %	5.6	5.1	7.5	5.5	6.4	6.4	6.5	5.7	6.5
Or	94.1	94.7	91.7	94.0	93.2	93.4	93.1	94.0	93.3
An	0.3	0.2	0.8	0.5	0.4	0.2	0.4	0.3	0.2

Average chemical composition of white K-feldspar from individual samples, determined by electron microprobe. Total iron is expressed as FeO.

salts. The precipitated nitrate salts were dissolved in 2N HCl, and ion-exchange resin columns were used to obtain a pure $PbCl_2$ solution. All operations were performed in clean-air laminar-flow hoods. The lead chloride solutions were mounted on single filaments in a silica–phosphate mixture. Total lead blanks for the feldspar samples are 1 ng. Fractionation corrections calculated from the isotopic standard NBS SRM 981 are 1.002907 for $^{206}Pb/^{204}Pb$, 1.00411 for $^{207}Pb/^{204}Pb$, and 1.006506 for $^{208}Pb/^{204}Pb$. Error limits calculated from repeated analyses of standards are $\sigma x = 0.021\%$, $\sigma y = 0.026\%$, $\sigma z = 0.029\%$ (where x, y and z refer to the above three ratios).

CHEMICAL COMPOSITION OF THE K-FELDSPAR

Broken Hill

Table 1 shows the representative analytical data collected in this study and by previous investigators. The data obtained by X-ray fluorescence indicate a higher Na content in view of the impossibility of removing albite impurities. However, the effect of such impurities on the quoted contents of lead and barium is negligible. The microprobe and XRF data on lead contents are in good agreement with published information on Broken Hill material (Čech *et al.* 1971, Plimer 1976, Hofmeister & Rossman 1985).

The amazonite in E9155 ranges from Or_{90} to Or_{95} (microprobe data; see Table 2); Fe, Mg, Ba and Ca are either very low or negligible. The lead content of the amazonite is high, ranging from 1 to 2 wt.%

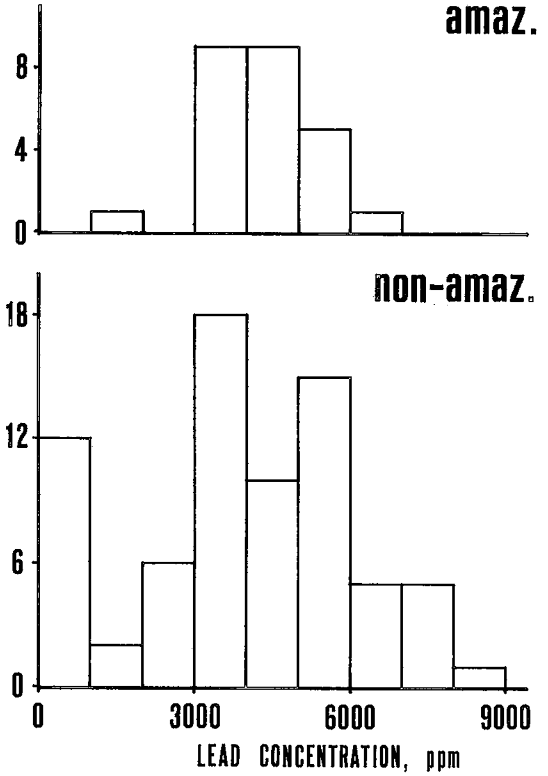

FIG. 2. Histogram showing the frequency distribution of lead concentration in K-feldspar from the Geco suite. Amazonitic and non-amazonitic K-feldspar was analyzed; the data indicate that white K-feldspar may contain as much or more lead than amazonitic K-feldspar. The lone sample of amazonite that contains between 1000 and 2000 ppm Pb is enclosed in galena. Ordinate: number of samples analyzed.

(average 1.51%). Spots selected for analysis by microprobe are free of galena (Fig. 1). These compositions seem to be the most Pb-enriched recorded. Čech *et al.* (1971) listed the lead content of a number of amazonite samples, the highest being an amazonite from Pack, Austria (1.35% Pb).

Electron-microprobe analyses across the retrograde rim reveal a distinct decrease in lead content of the feldspar from the amazonite (1.3 - 1.5% Pb) through the white halo around galena inclusions to the retrograde zones (60 - 2460 ppm Pb). Furthermore, a turbid, grey K-feldspar within the massive galena ore contains only 1140 ppm Pb compared to 13000 ppm in the nearby amazonite. Table 2 lists the compositions recorded at the sites indicated in Figure 1. The loss of lead and of the green color occurs only in areas that appear to have undergone a retrograde structural modification (see below).

TABLE 5. COMPOSITION OF K-FELDSPAR FROM MANITOUWADGE

	30-4	10-16	6F	6D	10A1
SiO_2 wt.%	65.37	65.96	64.37	64.39	67.10
Al_2O_3	18.77	18.69	18.92	18.88	17.27
Fe_2O_3	0.03	0.04	0.06	0.08	0.04
CaO	0.14	0.10	0.15	0.11	0.13
Na_2O	2.48	2.57	1.84	1.23	1.14
K_2O	13.04	12.68	13.89	14.65	13.57
P_2O_5	0.01	0.01	0.03	0.03	0.01
BaO	0.06	0.02	0.08	0.07	0.06
SrO	0.01	0.01	0.02	0.02	0.02
PbO	trace	trace	0.52	0.53	0.45
total	99.91	100.08	99.88	99.99	99.79
Pb ppm	74	108	4802	4904	4214
Ab mole %	22.1	23.3	16.5	11.2	11.2
Or	76.5	75.7	82.0	87.7	87.4
An	1.4	1.0	1.5	1.1	1.4

Bulk composition determined by X-ray fluorescence. Total iron expressed as Fe_2O_3.

Geco

The chemical compositions of amazonite (Table 3) and white K-feldspar (Table 4) are consistent and range from Or_{89} to Or_{97}, with sample averages from Or_{92} to Or_{95}. Calcium content is negligible in all cases. The Ba content is highly variable (0 to 8000 ppm), although the majority of the grains contain less than 1000 ppm. Associated white K-feldspar and amazonite contain a similar concentration of barium.

The average Pb contents of the K-feldspar are illustrated in histogram form (Fig. 2). The general trend defined by the white K-feldspar is mimicked by that of the amazonite. This is good evidence that whereas lead may play a role in the formation of the amazonite color, it is not the determining factor. The amazonite samples are concentrated in the middle range of the histogram, revealing that in many cases at Geco, pink or white K-feldspar is just as rich if not richer in lead. However, it is true that the amazonite color occurs at Geco only if the lead content exceeds 1000 ppm.

The XRF data on K-feldspar (Table 5) are in quite good agreement with the microprobe data. Albite lamellae and small grains of plagioclase in the separate account for the difference. The small amount of sodic feldspar dilutes the measured Pb concentration only slightly.

Samples 10–16 and 30–4 are fist-sized crystals of pink-white K-feldspar taken from pegmatite dykes distal to the orebody. The samples contain up to 23% albite owing largely to perthitic lamellae and sodic plagioclase included in the K-feldspar. Of particular note is the much lower Pb content of the two samples of pink-white K-feldspar, 108 and 74 ppm.

There is no compositional zoning in K-feldspar with respect to Na, K, Ba or, generally, lead. One exception is discussed here. In many cases where core and rim areas of amazonite and white K-feldspar grains were analyzed (or grains proximal and distal to galena where grain size is small), the lead content decreases where the feldspar is adjacent to galena

TABLE 6. Pb CONTENT OF K-FELDSPAR VERY CLOSE TO ("RIM") AND REMOVED FROM ("CORE") CONTACT WITH GALENA

sample number	"core"	"rim"
6F	5155	2350
	5060	2220
10B20	5230	2850
	6250	1890
6AD	3797	3440
6AP	5930*	160
	6530*	240
	4560	2980
	5410*	760
10AO	3133	2840
	3920	3700
	4290	2510
6D	2420	1360
	6490	6370
	3910	1840
	4710	4670

* indicates discrete grains of K-feldspar, one adjacent to and one removed from a grain of galena. Concentrations of Pb in ppm.

(Table 6). In each case the decrease in lead content occurs over a small distance. Only those parts of the feldspar directly adjacent to the galena are affected, and there is no visible physical alteration of the feldspar there. The galena is found either in fractures or is interstitial to the feldspar grains. One possible explanation for this phenomenon is that the interface between the feldspar and galena may have been physically open owing to unequal shrinkage during cooling, thus allowing very local retrograde equilibration. This could involve removal of lead from the feldspar and its transfer to the fluid phase responsible for the supply of sulfur and deposition of the galena.

As already noted, both white and green K-feldspar may have a high content of lead. There are also individual grains of amazonite that vary in color from white to green. This zonation is never concen-

TABLE 7. CELL PARAMETERS AND INDICATORS OF COMPOSITION AND DEGREE OF Al-Si ORDER, K-FELDSPAR FROM BROKEN HILL, AUSTRALIA

	a	*b*	*c*	α	β	γ	*V*	*a**	*b**	*c**	α*	β*	γ*	$t_1 0$	Or	Pb	
BH3	8.5732	12.9693	7.2128	90	116.036	90	720.59	0.129816	0.077105	0.154301	90	63.964	90	0.458	98.9	2795	OR
	0.0011	0.0016	0.0009		0.011		0.13	0.000020	0.000010	0.000018		0.011			93.5		
BH4	8.5708	12.9812	7.2023	90	116.028	90	720.04	0.129845	0.077035	0.154517	90	63.972	90	0.405	97.8	12919	OR
	0.0007	0.0008	0.0005		0.006		0.07	0.000014	0.000005	0.000010		0.006			92.0		
BH6	8.5637	12.9852	7.2018	90	116.027	90	719.63	0.129951	0.077011	0.154525	90	63.973	90	0.398	98.7	18081	OR
	0.0014	0.0022	0.0013		0.014		0.17	0.000026	0.000017	0.000026		0.014			90.9		
BH7	8.5684	12.9763	7.2149	90	116.015	90	720.92	0.129867	0.077063	0.154229	90	63.985	90	0.456	102.1	10163	OR
	0.0012	0.0017	0.0010		0.011		0.14	0.000019	0.000010	0.000019		0.011			94.4		
BH10*	8.570	12.987	7.209	90	116.000	90	720.91							0.421		11100	OR
	0.004	0.003	0.003				0.57								94.4		
E9155	8.5797	13.0043	7.2013	90	116.022	90	722.02	0.129703	0.076898	0.154529	90	63.978	90	0.371	103.5	15500	OR
(1)	0.0017	0.0028	0.0012		0.016		0.17	0.000028	0.000016	0.000020		0.016			97.5		
E9155	8.5651	12.9904	7.1989	90	116.017	90	719.81	0.129917	0.076980	0.154574	90	63.983	90	0.388	91.0	12000	OR
(2)	0.0005	0.0008	0.0004		0.004		0.05	0.000007	0.000005	0.000009		0.004			91.4		
E9155	8.5662	12.9805	7.2040	90	116.016	90	719.87	0.129901	0.077039	0.154462	90	63.984	90	0.418	91.2	12000	OR
(3)	0.0007	0.0009	0.0006		0.006		0.07	0.000013	0.000006	0.000012		0.006			91.6		
BH15	8.5761	12.9952	7.2084	90	116.072	90	721.62	0.129813	0.076951	0.154443	90	63.928	90	0.415	96.1	30000	OR
	0.0014	0.0032	0.0014		0.015		0.20	0.000027	0.000019	0.000027		0.015			96.4		
NBH2	8.5696	12.9928	7.2006	90	116.009	90	720.54	0.129841	0.076966	0.154528	90	63.991	90	0.384	100.6	?	OR
	0.0005	0.0007	0.0004		0.005		0.05	0.000007	0.000004	0.000009		0.005			93.4		
KLW-V4	8.5942	13.0009	7.2084	90	116.054	90	723.57	0.129519	0.076918	0.154419	90	63.946	90	0.389	104.8	?	OR
	0.0017	0.0031	0.0011		0.014		0.19	0.000027	0.000019	0.000023		0.014			102.0		
BH13	8.5852	12.9605	7.2197	90.578	115.969	87.920	721.72	0.129644	0.077210	0.154070	90.370	64.034	92.032	0.945	96.4	?	LM
	0.0007	0.0009	0.0006	0.010	0.006	0.010	0.07	0.000011	0.000006	0.000012	0.009	0.006	0.009		97.5		
BH14	8.5806	12.9646	7.2144	90.468	115.955	88.195	721.24	0.129677	0.077173	0.154163	90.359	64.047	91.780	0.862	95.0	?	IM
	0.0010	0.0012	0.0007	0.013	0.010	0.015	0.10	0.000016	0.000007	0.000017	0.013	0.010	0.015		95.3		

Specimens BH3, E9155(3), BH13 and BH14 consist of grey-white K-feldspar; the others are amazonitic. OR orthoclase, IM intermediate microcline, LM low microcline. Lead concentration quoted in ppm. Units: *a*, *b*, *c* in Å, *V* in $Å^3$, *a**, *b**, *c** in $Å^{-1}$, α, β, γ, α*, β*, γ* in degrees, Or in %. Or content quoted on first line is Or(*b*c**), calculated using the expression of Blasi (1977). Or content quoted on second line is Or(*V*), calculated using the expressions of Kroll & Ribbe (1983), for the series LA - LM in the case of BH13 and for intermediate degrees of Al-Si order in all other cases. * Cech et al. (1971).

TABLE 8. CELL PARAMETERS AND INDICATORS OF COMPOSITION AND DEGREE OF Al-Si ORDER, K-FELDSPAR FROM GECO, ONTARIO

	a	*b*	*c*	α	β	γ	*V*	*a**	*b**	*c**	α*	β*	γ*	$t_1 0$	Or	Pb	
30-4	8.5760	12.9638	7.2244	90.683	115.944	87.652	721.63	0.129775	0.077204	0.153935	90.382	64.062	92.279	1.010	101.6	74	LM
	0.0008	0.0011	0.0006	0.010	0.009	0.009	0.08	0.000013	0.000006	0.000014	0.010	0.007	0.009		97.2		
10A1	8.5743	12.9655	7.2226	90.664	115.970	87.647	721.23	0.129831	0.077195	0.154009	90.407	64.035	92.293	1.002	100.6	4214	LM
	0.0010	0.0011	0.0010	0.009	0.009	0.009	0.10	0.000016	0.000007	0.000020	0.009	0.009	0.010		96.1		
6D	8.5665	12.9641	7.2207	90.677	115.954	87.648	720.41	0.129931	0.077203	0.154028	90.391	64.051	92.286	0.997	99.9	4909	LM
	0.0011	0.0012	0.0008	0.011	0.009	0.009	0.10	0.000019	0.000007	0.000016	0.011	0.009	0.009		93.7		
6F	8.5720	12.9602	7.2222	90.670	115.952	87.680	720.83	0.129843	0.077225	0.153995	90.384	64.053	92.254	1.001	99.6	4802	LM
	0.0006	0.0009	0.0005	0.008	0.006	0.006	0.07	0.000010	0.000005	0.000010	0.009	0.006	0.007		94.9		
Geco	8.5706	12.9651	7.2173	90.667	115.946	87.657	720.52	0.129860	0.077197	0.154090	90.398	64.059	92.281	0.984	98.7	3900	LM
	0.0014	0.0026	0.0011	0.021	0.016	0.020	0.18	0.000025	0.000016	0.000028	0.020	0.016	0.020		94.1		

Specimen 30-4 is white; the others are amazonitic. The specimen labeled "Geco" was donated by F. Bakker, and its Pb content was determined by spectrographic analysis by Nancy Conklin of the U.S. Geological Survey in Denver. Or(*V*) is calculated using the expression of Kroll & Ribbe (1983) for the series LA - LM. Units and symbols are the same as in Table 7.

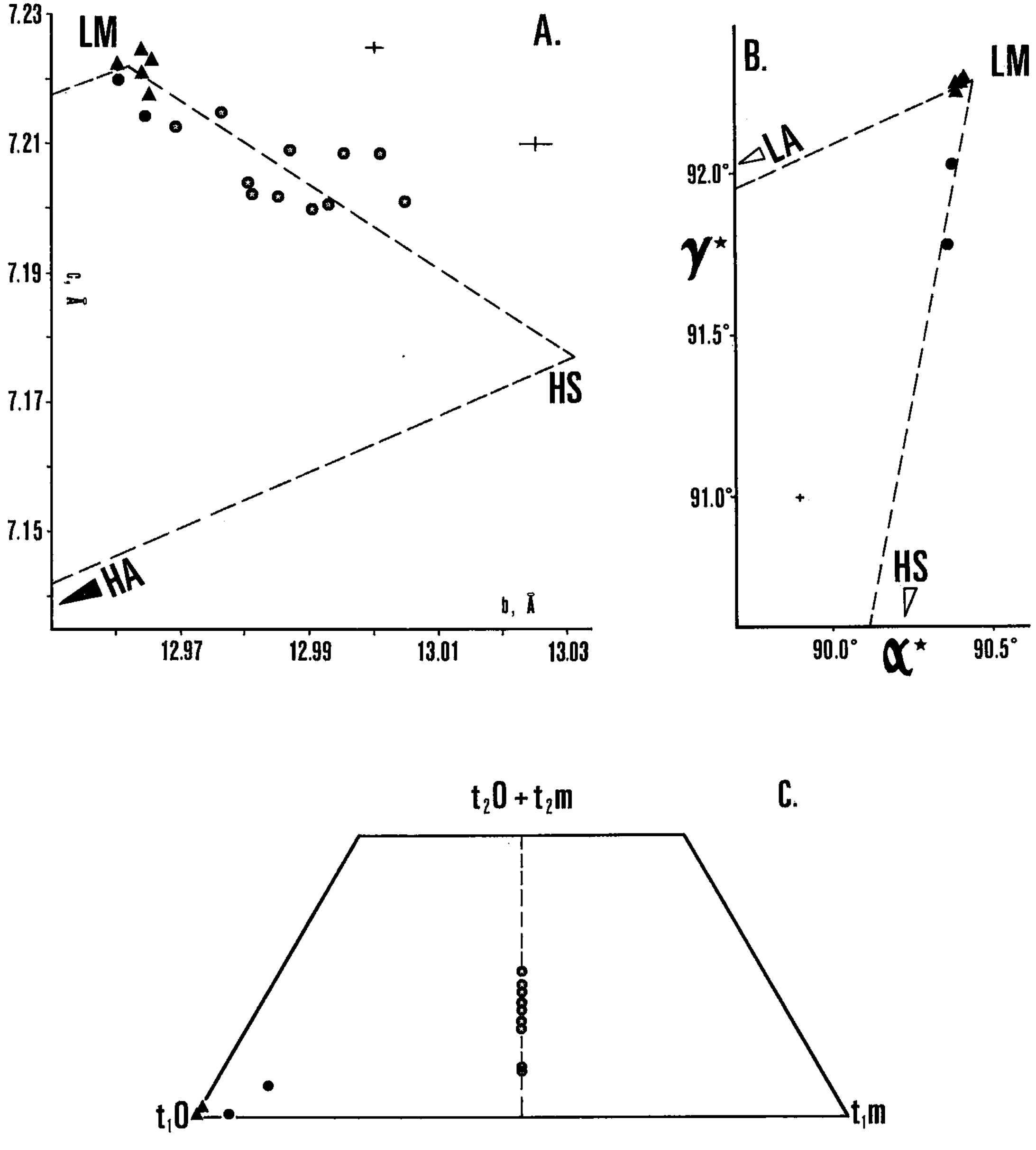

Fig. 3. A. Plot of the cell dimensions *b versus c* for the eighteen samples of K-feldspar included in this study. The five data-points representing low microcline from Geco (black triangles) plot close to the LM (low microcline) corner of the *b* - *c* quadrilateral. Two samples of microcline also form part of the Broken Hill suite (black dots). Most of the K-feldspar at Broken Hill is orthoclase (starred black dot); these data points illustrate a large variability in the degree of Al–Si order attained in orthoclase, reflecting degree of recrystallization above a temperature of 400°C. HS high sanidine, HA high albite. Two sets of error bars are shown, one referring to the low microcline data-points, the other to the orthoclase data-points. B. Plot of the interaxial angles α^* and γ^* for the triclinic samples (all samples of monoclinic K-feldspar plot at $\alpha^* = \gamma^* = 90°$). Triangles: Geco suite, black dots: Broken Hill suite. HS high sanidine, LM low microcline, LA low albite. This plot indicates that the microcline from Broken Hill, formed in an evolving retrograde environment, is clearly less well ordered than that in the Geco orebody. C. Part of the triangular plot $t_1O - t_1m - (t_2O + t_2m)$, showing the important differences between the K-feldspar at Broken Hill, in which $t_1O = t_1m$ in most cases and in which the microcline falls short of end-member low microcline ($t_1O = 1$). The symbols are the same as in A and B.

tric, but up to half the crystal may be green, and may grade to white in the other half. In a few cases the amazonite is mottled green and white. Grains of such color-zoned amazonite were analyzed by electron microprobe. The results show that both green and white portions of the same crystal have similar contents of lead: *e.g.*, 6F (white) 4010 ppm and 6F (green) 4420 ppm. The difference in lead content barely exceeds analytical error. The change in color is likely due to some other factor than Pb content because the difference in lead content is no greater than the variation found in other grains of amazonite that are uniformly colored. The H_2O content may be lower in the white portion (Hofmeister & Rossman 1985).

X-RAY-DIFFRACTION STUDY

Six samples of K-feldspar were chosen from the Broken Hill suite for an X-ray-diffraction study. Data from six other refinements (R.F. Martin, unpubl. data) and the results of Čech *et al.* (1971) are also plotted. Four samples of K-feldspar from Geco were selected; three are amazonite (6D, 6F, 10A1) and one is pink (30–4). A fifth refinement of amazonite was carried out on a sample contributed by F. Bakker. Cell edges, angles, ordering parameters and lead content are listed in Tables 7 and 8.

The refinements for the Broken Hill samples confirm previous work in that the amazonite is orthoclase (definition of Ribbe 1983). The white or pink K-feldspar, however, may be more ordered (low microcline, intermediate microcline or orthoclase). As noted previously, the grid twinning in the Geco samples indicates a triclinic structure, and the XRD results confirm the absence of orthoclase. The samples from both suites range from nonperthitic to microperthitic, and this is confirmed by the absence or relative weakness of the albite peaks in the XRD study.

Plots of b *versus* c and α^* *versus* γ^* (Figs. 3A,B) were made to determine the degree of Al–Si order in the samples. Values of $\Delta(bc)$ and $\Delta(\alpha^*\gamma^*)$ were calculated using the approach of Blasi (1977) and, from these values, t_1O was calculated (Tables 7, 8). Regardless of color or lead content, the samples from Geco form a tight cluster around the low microcline end-member (Figs. 3A, B, C). The Broken Hill data reveal a relatively large spread in the degree of Al–Si order; the orthoclase samples show a spread in t_1O from 0.38 to 0.46, and a small difference in degree of order exists between the low microcline and the intermediate microcline. For the orthoclase, this indicates that the mineral had locally progressed toward the monoclinic–triclinic inversion before final retrograde equilibration. However, the retrograde conversion to low microcline evidently did not proceed in many cases. Also, all samples of Broken Hill amazonite consist of orthoclase, whereas the triclinic K-feldspar is non-amazonitic. However, it is evident from the two suites that amazonite exists in both triclinic and monoclinic structures.

Values of Or content calculated from b^* and c^* for Broken Hill (91–103%) and Geco (99–101%) (Tables 7,8) indicate that the K-feldspar from both localities is rather potassic, in agreement with the nonperthitic to microperthitic nature of the samples. The samples have equilibrated successfully to a low temperature, and more so at Geco than at Broken Hill. Values greater than 100% (Tables 7, 8) indicate that a large cation like Rb, Cs and Pb(?) causes a slight expansion in b^* and c^*. Compositions determined by electron microprobe (Tables 2–4) are very similar to those inferred by XRD data; the small differences probably reflect the influence of the same large cations on the cell dimensions.

The presence of low microcline and the well-developed grid twinning at Geco are indicative of relatively slow cooling in the presence of an aqueous fluid that catalyzed the inversion. Such conditions are characteristic of a pegmatite system. The persistence of orthoclase at Broken Hill, then, appears somewhat uncharacteristic of pegmatites; the range of Al–Si order found amongst the Broken Hill samples requires closer scrutiny. The low microcline sample (BH14) is a fine-grained pink K-feldspar that rims and penetrates coarser crystals of grey-white K-feldspar along fractures and cleavages. The distribution of the pink microcline suggests that it results from the modification of the grey-white K-feldspar, which is intermediate microcline. If the fluid phase that produced the low microcline rim on the intermediate microcline had interacted with the widespread orthoclase at Broken Hill at a temperature less than 400°C (approximate temperature of the monoclinic – triclinic inversion), then we could

TABLE 9. LEAD-ISOTOPE DATA FOR K-FELDSPAR AND GALENA FROM BROKEN HILL

			$\frac{^{206}Pb}{^{204}Pb}$	$\frac{^{207}Pb}{^{204}Pb}$	$\frac{^{208}Pb}{^{204}Pb}$
Amazonite	1	BH4	16.011	15.392	36.668
	2	BH6	16.013	15.396	35.698
		repeat	16.012	15.396	35.690
	3	BH7	16.015	15.399	35.693
		repeat	16.015	15.399	35.707
	4	BBH	16.002	15.387	35.667
	5	E9155	16.004	15.386	35.668
		repeat	16.004	15.388	35.681
White K-feldspar	6	BH3	16.045	15.389	35.677
Galena	7	BH1	16.004	15.388	35.672
	8	NBH1	16.005	15.393	35.684
	9	NBH2	16.049	15.395	35.735
		repeat	16.048	15.395	35.739
	10	BH6	16.032	15.395	35.698
	11	BH7	16.010	15.391	35.679
	*	JRR	16.005	15.389	35.651

* Broken Hill standard from J.R. Richards (pers. comm. to G.L. Cumming). Concerning the galena samples, BH1 is from the main orebody, NBH1 is from the north orebody, NBH2 is suspect, BH6 and BH7 are disseminated in the pegmatite.

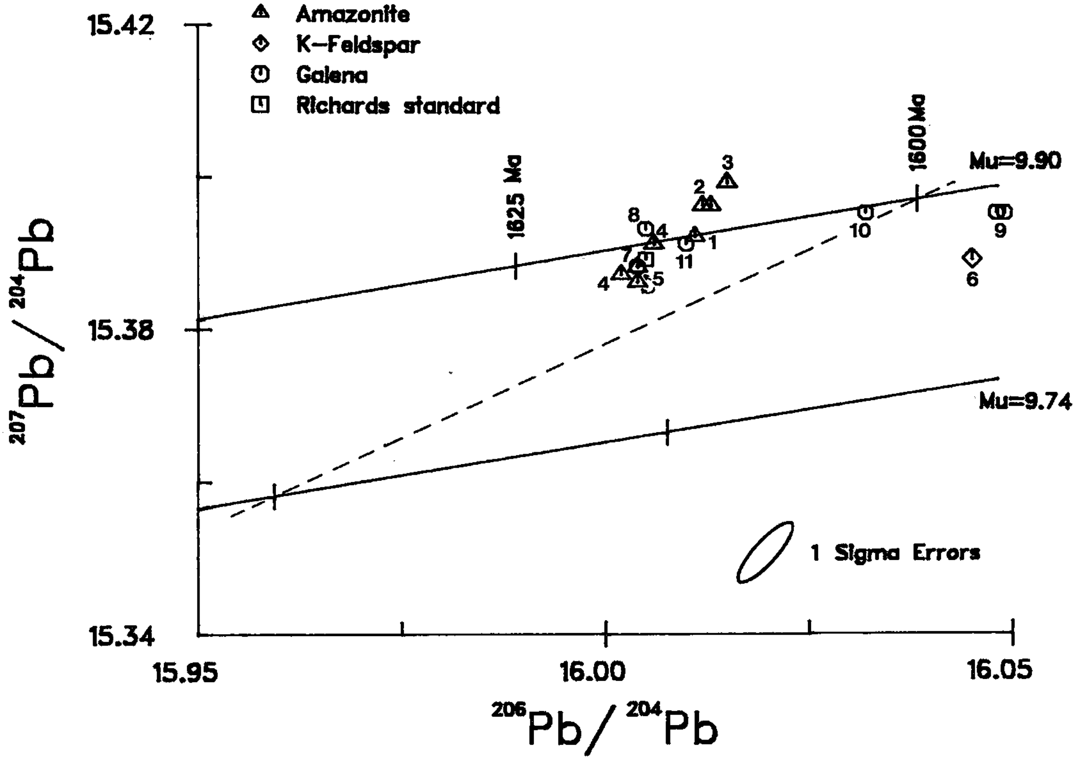

FIG. 4. A plot of the ratios ^{207}Pb/^{204}Pb *versus* ^{206}Pb/^{204}Pb for common lead in samples of amazonitic orthoclase, white orthoclase and galena from Broken Hill. The standard of J.R. Richards (pers. comm. to G.L. Cumming) is added for comparison. The data for the amazonite and most of the data for galena cluster about this value (indicating approximately 1612 Ma). The solid lines are growth curves for different values of ^{238}U/^{204}Pb (Mu) calculated according to Stacey & Kramers (1975). The dashed line is a 1600-Ma isochron. The numbers are those used in Table 9.

expect efficient ordering of the monoclinic K-feldspar to microcline. In the extreme case, recrystallization would result in the perfectly ordered structure of low microcline, as is virtually achieved in the pink rim at Broken Hill, and possibly in the removal of lead from the feldspar structure (as noted previously). This would in turn cause a discoloration of the amazonite and formation of disseminated galena in the altered areas if sulfur were locally available. We contend that at Geco, the ordering is complete on a regional scale; the relative scarcity of amazonite there may indicate that the hydrothermal fluid present during the ordering reaction did contain the necessary anions to remove the lead in almost all cases.

LEAD-ISOTOPE GEOCHEMISTRY

Broken Hill

To compare the isotopic composition of lead in amazonite, galena and white K-feldspar, we analyzed five samples of amazonite, five of galena and one sample of grey-white orthoclase (Table 9). Samples BH3, 4, 5, 6 and 7 are high-purity mineral separates, whereas BBH and E9155 are chip samples. Galena samples BH6 and 7 were separated from the same rock as amazonite BH6 and 7, and are interstitial to the amazonite. Galena samples BH1, NBH–1 and –2 are derived from massive ore in the Lode horizon.

Plotted with the results (Fig. 4) is a value for Broken Hill galena determined by J.R. Richards (G.L. Cumming, pers. comm. 1984) that is similar to the accepted composition for the Broken Hill system, quoted by Stacey & Kramers (1975). All of the amazonite data-points and most of the galena data-points cluster around the value of Richards. The trend of the cluster is exactly that of the error ellipse. Using a two-stage growth curve for a ^{238}U/^{204}Pb value of 9.90, the results indicate an age of resetting of the galena–amazonite system of approximately 1625 Ma (Fig. 4). Note that the chip samples (4, 5) also plot in the cluster and are even slightly less radiogenic than the galena and other amazonite, but still within error. Three samples plot significantly outside the cluster: two represent galena (BH6, NBH–2) and one is the grey-white orthoclase (BH3). Replicate analyses of several samples indicate that the measurements are reproducible within error.

Geco

Mineral separates of amazonite (6F, 6D, 10A1) and white K-feldspar (6P, 10–16, 30–4) were analyzed, along with a sample of galena randomly chosen from the orebody. Sample 6P was leached with HCl, HNO_3 and HF to produce three additional samples. The results (Table 10, Figs. 5, 6) use the growth curve of Stacey & Kramers (1975). The model ages for the galena are calculated according to the two-stage model of Stacey & Kramers (1975).

The first leach from sample 6P [6P–L1(5)] is enriched in radiogenic lead compared to the rest of the data (Fig. 5). This fraction presumably contains the lead generated by U decay in the vicinity of the sampling site. In Figure 6, note how closely the data from amazonite and galena overlap. Also, the amazonite points overlap despite the separate occurrence of 10A1 and 6D, F. The samples of white K-feldspar (6P, 10–16, 30–4) are somewhat scattered. The subsamples of 6P (6P–L1, 6P–L2 and 6P–R) define a linear trend (Fig. 5) that corresponds to an age of 2726 ± 25 Ma. Specimens 10–16 and 30–4 are not included in the regression, as they are derived from different pegmatites. The model age for the amazonite and galena clusters are about 2700 Ma, which is the accepted age of the rocks in the Manitouwadge area (Stacey & Kramers 1975).

DISCUSSION

Although these two occurrences are separated by thousands of kilometres and some 1100 Ma, they are quite similar in many ways. Both deposits are stratiform massive-sulfide deposits that have undergone high-grade metamorphism and at least two phases of deformation. Pegmatites of probable anatectic origin are common to both areas, and where these pegmatites are associated with the orebodies, they may contain amazonite. These similarities argue strongly for a similar environment of formation of the amazonite in the two suites. The environment must allow for the presence of lead in the pegmatites and the K-feldspar and explain the similar isotopic composition of the lead in the amazonite and galena. The hypothesis should also explain why Pb, normally chalcophile, substitutes in a silicate mineral in close proximity to an ore deposit (where there is an abundance of sulfur).

Chemistry

Our results on the composition of the K-feldspar from both suites substantiate the findings of Foord & Martin (1979) and others in that amazonite contains high amounts of lead. In the two suites examined, no amazonite with less than 1000 ppm Pb was found.

The correlation noted between intensity of coloration and lead content (Foord & Martin 1979) is evident in both suites. A decrease in Pb content and a change in color occur in altered portions of the amazonite, which may or may not contain galena. This is best seen in the "altered" amazonite from Broken Hill. However, the trend is also apparent among unmodified samples. A dark green amazonite typically contains more lead than a pale green one. For example, pale amazonite at Geco contains on average 0.48% Pb, whereas the emerald green amazonite from Broken Hill contains 1.51% on average. Apparent exceptions to this correlation are found at Geco. The amazonite-bearing pegmatites of Geco are, overall, Pb-rich. Even the fine-grained white K-feldspar in the pegmatite matrix may contain in excess of 1000 ppm lead. However, on a broader scale, K-feldspar in pegmatites not in contact with the orebody and lacking amazonite contains less than 100 ppm Pb (*e.g.*, 10–16, 30–4).

In light of the findings of Hofmeister & Rossman (1985), the occurrence of fine-grained Pb-rich (greater than 1000 ppm) white K-feldspar in both suites may result from an insufficient amount of structurally bound water to form the necessary Pb – H_2O pair required for the color centre. However, the mode of formation of coarse-grained, Pb-rich white K-feldspar (BH3) or mottled green-and-white amazonite (6F) remains an enigma. Their lack of color could stem from insufficient or excess natural irradiation (Hofmeister & Rossman 1985) or, again from a lack of Pb – H_2O pairs.

Degree of Al–Si order

Hofmeister & Rossman (1985) noted that increased lead content may promote increased disorder in K-feldspar, such that Pb-rich (2%) K-feldspar is monoclinic, and Pb-poor K-feldspar is triclinic. The high-Pb monoclinic amazonite at Broken Hill and

TABLE 10. LEAD-ISOTOPE DATA FOR K-FELDSPAR AND GALENA FROM GECO

			$\frac{^{206}Pb}{^{204}Pb}$	$\frac{^{207}Pb}{^{204}Pb}$	$\frac{^{208}Pb}{^{204}Pb}$
Amazonite	1	10A1	13.221	14.400	33.081
	2	6D	13.223	14.405	33.113
	3	6F	13.226	14.410	33.118
White K-feldspar	4	6P	13.562	14.479	33.279
	5	6P-L1	17.374	15.186	35.283
	6	6P-L2	13.665	14.483	33.281
	7	6P-R	13.312	14.423	33.131
	8	10-16	13.664	14.551	33.273
	9	30-4	13.819	14.616	33.361
Galena	10	grab	13.215	14.339	33.103

L1 leach in 6N HCl, L2 leach in HNO_3 with a few drops of concentrated HF, R residue.

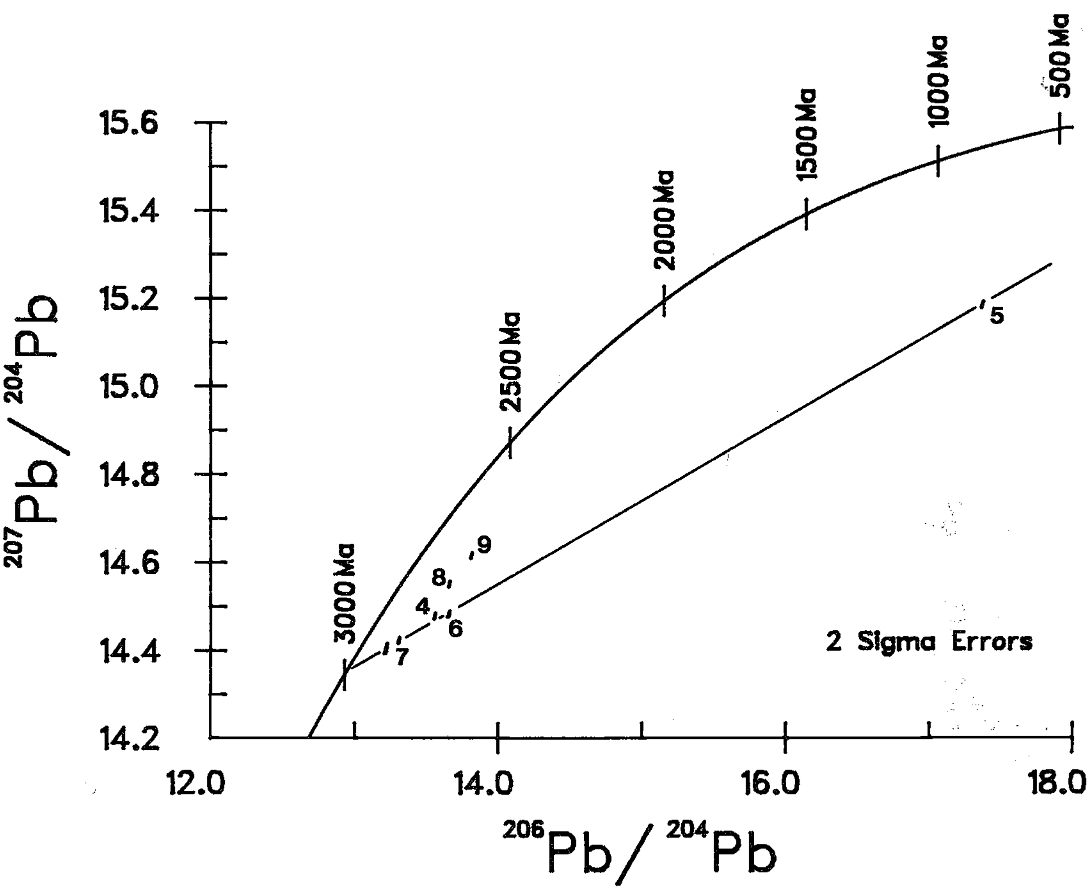

FIG. 5. A plot of the ratios ^{207}Pb/^{204}Pb *versus* ^{206}Pb/^{204}Pb for common lead in samples of amazonitic microcline, white microcline and galena from the Geco deposit, Manitouwadge district. The numbers are those used in Table 10. The isochron, based on leaches from sample 6P, gives an age of 2726 ± 25 Ma. The growth curve is from Stacey & Kramers (1975).

the lower-Pb triclinic amazonite at Geco could be construed as evidence for the above correlation. However, the fact that Pb-poor K-feldspar at Geco has the same degree of order as its amazonitic counterpart argues against the Pb – degree of order correlation. Rather, the difference in degree of order between the Broken Hill and Geco amazonite is attributed to differing thermal histories and degrees and timing of fluid interaction.

In bulk compositions such as these, plutonic K-feldspar crystallizes from the melt in the disordered, monoclinic form, and begins to order (and unmix) during cooling by interaction with a fluid medium. If cooling proceeds slowly and if the fluid medium is available to catalyze the process below 400°C, then the ordering reaction will go to completion, such as at Geco. However, if the cooling period is terminated rather abruptly, possibly as a result of uplift, or if the fluid catalyst is present only when the crustal block is above 400°C, then the K-feldspar may order part way but remain metastably in the monoclinic form, such as is found in the Broken Hill pegmatites. There, introduction of a fluid medium during the cooling of the pegmatites or during the mild Early Paleozoic thermal event resulted in the local conversion of orthoclase to intermediate microcline and, very locally, to incompletely ordered low microcline.

The occurrence of galena in the modified areas of the Broken Hill amazonite and in fractures in Geco amazonite, along with a decrease in lead content of the amazonite in contact with the galena, reflect a re-equilibration of the Pb-bearing K-feldspar with later sulfur-bearing fluids.

Isotopic implications

The close relationship between "primary" galena

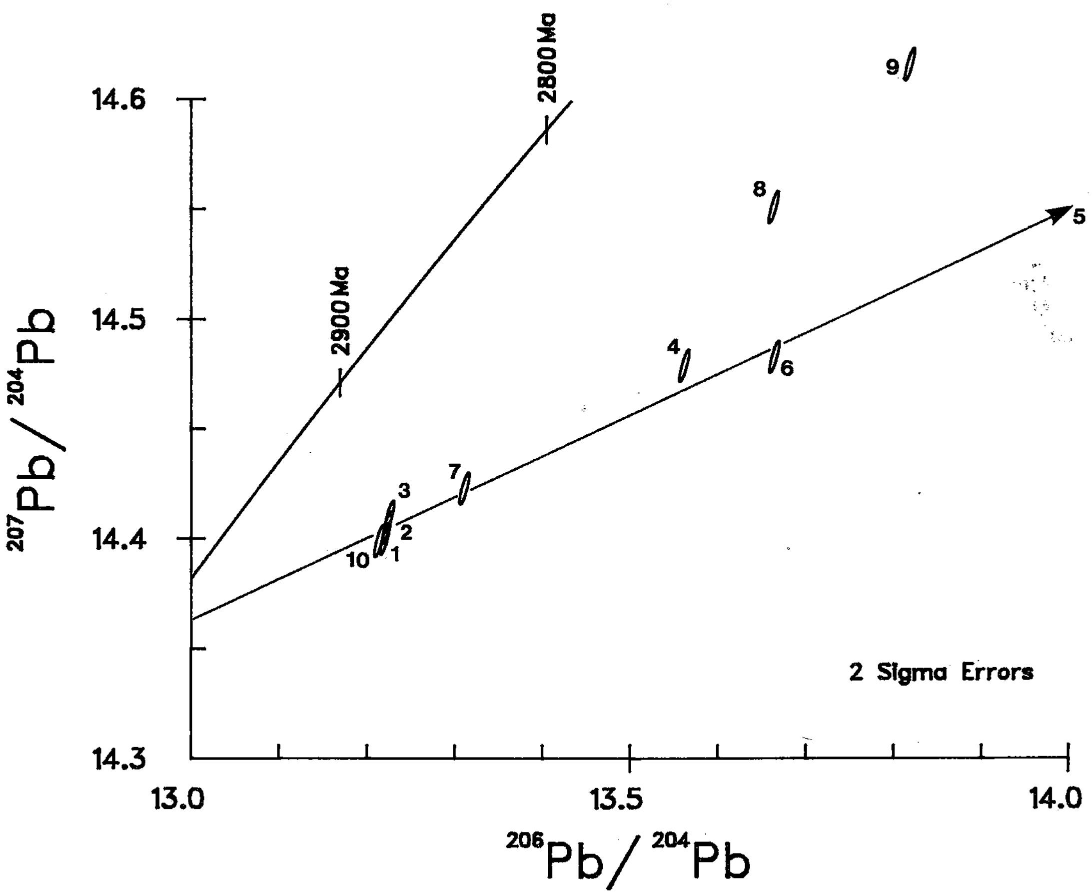

FIG. 6. Expanded view of plot shown in Figure 5 to clarify relationships in the lower part of the isochron. Note that the amazonite and the galena overlap, but the white microcline is more radiogenic. The sample numbers are those used in Table 10.

and amazonite is reflected in their similar Pb isotope composition. In the Geco samples there is a complete overlap of amazonite and galena. Similarly, all but two galena samples from Broken Hill plot within error of the amazonite. These findings indicate that the ordering reaction, which involved H_2O, was largely a closed-system process with respect to the lead isotopes. The data on the amazonite and the bulk of the galena are consistent with previously reported compositions of galena from Broken Hill and Geco (Stacey & Kramers 1985, Oversby 1978, Franklin & Thorpe 1982, Franklin *et al.* 1983). This is a strong indication that the pegmatites and their constituent amazonite, which postdate the orebodies, derive their lead from the orebodies. Furthermore, the white K-feldspar, generally poorer in lead than in the amazonite, is more radiogenic than the amazonite and the orebodies (*e.g.*, BH3, 10–16, 30–4, 6P).

The orebodies respond to metamorphism through recrystallization and remobilization of sulfides if there is accompanying deformation (Vokes 1969); here, "remobilization" should not be construed to indicate that melting of the sulfide assemblages has occurred (Plimer 1984). The flow of sulfides at Geco is demonstrated by the shearing-off of once cross-cutting pegmatites by remobilized ore (Suffel *et al.* 1971). Prograde metamorphic reactions produce fluids through the dehydration and decarbonation of phases in and near the orebodies. The fluids would likely be a mixture of H_2O, CO_2 (Aines & Rossman 1984) and, most likely, H_2S, F and Cl as well. Circulation of these fluids aid recrystallization and result in extensive transport and redistribution of base metals in the orebody and, locally, in the wall rock as well.

In a study of melting relations involving PbS, FeS_2 and granite (+ H_2O), Kullerud & Yoder (1967) found that at a temperature of 650°C, neither sulfide phase had melted, but that extensive recrystallization had occurred, with pyrite replaced by pyrrhotite (S_2 lost), accompanied by extensive redistribution of galena and quartz *via* the vapor phase. At 725°C, melting of the granite occurred, and the resulting quenched melt was found to contain disseminated sulfides. The sulfide-bearing pegmatites in and around the Broken Hill and Geco deposits are believed to have formed in much the same manner, most likely by the *in situ* melting of metamorphosed sulfide-bearing pelitic and quartzofeldspathic material.

Such a setting for anatexis would explain a number of features. The amazonite-bearing stringers, whether in the orebody or in the surrounding gneisses, could be intruded from the site of melting. Coeval pegmatites formed outside the ore environment would be amazonite- and sulfide-free. Galena and amazonite would share the same isotopic composition because they both formed in the same Pb-rich environment. A more remote setting for anatexis, with "contamination" of the granitic melt only upon intrusion into the ore zone, is a less likely hypothesis, in our opinion. Considered even less likely is a proposal that the lead in amazonite is added at a subsolidus temperature (*cf.* Doe & Hart 1963). As the color is intrinsic and ultimately due to structural defects, there can be little driving force to induce such defects in a normal feldspar during its subsolidus evolution. In fact, we contend that thorough recrystallization of amazonite, such as in the Geco mine, will progressively remove the color centres.

The regression of isotopic data for the leach fractions from sample 6P (from the same pegmatite as amazonite 6F) and the amazonite gives an age of 2726 ± 25 Ma, close to the accepted age of 2700 Ma of the rocks in the Manitouwadge area. This indicates that the more radiogenic K-feldspar of this pegmatite had initially the same isotopic composition as the galena and amazonite, thus substantiating the proposal that anatexis occurred within the ore environment. The more radiogenic composition of sample 6P is then a direct artifact of its lower concentration of lead and open-system behavior during its recrystallization.

The other samples of white K-feldspar (10–16, 30–4) and those of Tilton & Steiger (1969) show considerable scatter. This could in part be due to the addition of radiogenic lead through U decay in nearby accessory minerals, and local "contamination" of the lead in the K-feldspar during the ordering reaction (see below). However, if an isochron of about 2700 Ma is drawn through any one of these points, an intersection with the ore lead is not possible. Assuming that the cross-cutting pegmatites at Geco are, broadly speaking, of the same age, this scatter in isotopic values may then reflect differing initial ratios inherited from their respective parental material. The presence of a large number of "pegmatite" bodies at Manitouwadge, with variable chemical and modal compositions, probably reflects the formation of small batches of anatectic magma in numerous localized sites rather than from a single magma-chamber. Each batch can have a slightly different lead-isotope signature owing to differing combinations of parental material and differing U/Pb values. The Broken Hill pegmatites can be described similarly.The Rb/Sr isotope values of K-feldspar from the pegmatites exhibit the same type of scatter (Shaw 1968), and plot above the isochron for the whole-rock gneiss samples; further study of the Pb-poor pegmatites of this suite may show that the lead isotopes behave similarly.

The grey-white orthoclase BH3 is taken from the same pegmatite as amazonitic orthoclase BH7, but contains a quarter of the amount of lead and is more radiogenic than BH7. The possibility exists here also that the isotopic composition of BH3 has somehow become more radiogenic, presumably through the decay of uranium in nearby accessory phases. However, it is doubtful that leaching of this sample will regress its composition toward the ore-lead values. Retrograde alteration of the sample by a fluid phase, however, could have resulted in exchange of lead and addition of a radiogenic component. Galena BH6 and NBH–2 may have been similarly affected, thus resulting in anomalous ratios. Galena BH6, for example, is from the same sample as amazonite BH6. The radiogenic nature of this galena may reflect the incorporation of "mixed" lead, removed from accessory phases as well as from the amazonite by a fluid phase during retrograde metamorphism.

The increase in the proportion of radiogenic lead in microcline may be a consequence of the feldspar – water interaction (local solution and redeposition) that leads to the increase in Al–Si order. It is conceivable that as monoclinic K-feldspar that is relatively lead-rich is converted to microcline, the net loss in lead is accompanied by an *ion exchange* of structurally bound lead with lead carried in the fluid medium. The lead that is preferentially retained in the structure probably is that present according to the coupled substitution $Pb^{2+} + Al^{3+} = K^{+} + Si^{4+}$, *i.e.*, lead that is considered "inactive" from the point of view of the formation of the amazonite color. This would provide an explanation for the common presence of radiogenic lead in samples of Precambrian microcline, and the finding of Ludwig & Silver (1977) that in no case are the observed U and Th contents sufficient to explain the buildup in the radiogenic component. Ludwig & Silver considered most of the radiogenic component "parentless", *i.e.*, it must have found its way into the feldspar from elsewhere in the rock.

Sulfide–silicate equilibria

The formation of amazonite depends on the contribution of lead from the orebodies. Lead, however, is chalcophile; the concentration of lead in a silicate mineral so close to a sulfur-rich environment requires an explanation. The breakdown of galena during metamorphism is a consequence of desulfurization, *i.e.*, loss of sulfur once the mineral becomes unstable. Evidence for desulfurization at Broken Hill stems from two assemblages. The first is a pyrrhotite envelope around the southern end of the orebodies. The envelope results from the desulfurization of pyrite by a lowering of the fugacity of sulfur during metamorphism (Plimer 1976). The second assemblage is a halo of magnetite, biotite and gahnite around the pyrrhotite envelope (Johnson & Klingner 1976). Work on the assemblage (E.J. Essene, pers. comm. 1984) reveals that gahnite and quartz (+ S_2) formed through the desulfurization of sphalerite in a reaction with sillimanite.

A pyrrhotite envelope may also exist around parts of the Geco deposits (E.J. Essene, pers. comm. 1984). Furthermore, gahnite is also found associated with the deposit. Gahnite at the Geco mine occurs largely in the enclosing cordierite - staurolite - biotite - garnet schists and results from the breakdown of zincian staurolite (Spry 1982). However, the observation of gahnite, sphalerite, muscovite and quartz in veins in pegmatites would seem to indicate that desulfurization of sphalerite also occurred during metamorphism (Stevenson 1985, Suffel *et al.* 1971).

The breakdown of galena in a fluid medium, then, requires a reduction in the fugacity of sulfur such that galena becomes unstable with respect to Pb^{2+} and a sulfur-bearing volatile species. Under minimum conditions for anatexis [650°C, $P(H_2O) = 5$ kbar], only a relatively small decrease in $f(S_2)$ below the pyrite–pyrrhotite boundary would be required for the galena to become unstable (Kajiwara 1970). During cooling, the fugacity of sulfur begins to increase in localized areas; the pore fluids may then scavenge lead from the K-feldspar during its recrystallization (*i.e.*, ordering and exsolution) and deposit it as fine-grained galena in fractures and along the rim of amazonite grains.

Differences in thermal history

Although the two suites share many characteristics, they differ significantly in their feldspar mineralogy. The Geco suite contains grid-twinned low microcline, as could be expected of a mesozonal crustal block that cooled very slowly and at a uniform rate from 650°C. Uplift of the Manitouwadge crustal block from a depth of 18 to 20 km probably occurred long after the effects of the Kenoran orogeny had ceased. Recrystallization of the primary K-feldspar was thorough during this protracted period of cooling, and amazonite was preserved only where ionic sulfide species were in short supply. Subsolidus compositional *and* structural equilibrium was attained in the K-feldspar at Geco, and relics of the original (or even a more evolved) monoclinic K-feldspar should not be expected.

In contrast, the Broken Hill pegmatites still retain the original high-temperature monoclinic structure, except where the effects of retrograde metamorphism or of the Early Paleozoic reheating have been important. Although the pressure and temperature attained in the Willyama crustal block are roughly comparable to those in the Manitouwadge block, the cooling history must have differed significantly. In particular, the K-feldspar was allowed to order above the field of stability of microcline, and this stage lasted at least 90 million years, according to Harrison & McDougall (1981), possibly on account of a rift-related environment and high heat-flow (Plimer 1985). This very slow rate of regional cooling was followed by sufficiently rapid cooling through this field (caused by rapid uplift?) that conversion to microcline could not be carried out efficiently, in spite of the presence of water (17, 22 and 35 ppm of structural water are noted in three samples of amazonitic orthoclase from Broken Hill, amounts that are completely comparable to the level of structural water present in amazonitic microcline; Hofmeister & Rossman 1985). The high-temperature assemblage can still be found and, by implication, so can the original textures and mineral assemblages in the ore zone. Although compositional equilibration was attained in the K-feldspar (Table 7) *via* an ion-exchange process, structural equilibration was not. The Willyama block evidently escaped any significant event of regional metamorphic reheating after the 1660 Ma culmination that could have eliminated the relict high-temperature feldspar. The prominence of amazonite at Broken Hill reflects the relative unimportance of the retrograde effects and, possibly, a greater proportion of disseminated galena in the quartz- and feldspar-bearing metamorphic assemblage that underwent melting than at Geco. Whether or not the original orthoclase at Geco was as lead-rich as at Broken Hill remains unanswered. The presence of amazonite in pegmatites in medium- to high-grade metamorphic terranes can be considered a useful indicator of potential base-metal mineralization, although from our findings, it seems restricted to the immediate vicinity of the mineralized zone.

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