Distribution of germanium in rocks and minerals of the Ilímaussaq alkaline complex, South Greenland

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In the agpaitic nepheline syenites of the Ilímaussaq complex, analyses by X-ray fluorescence spectrometry reveal that Ge is largely held in arfvedsonite (2.4–4.3 ppm) and aegirine (2.5–4.3 ppm) and has abnormally low contents (down to < 0.2 ppm) in microcline. This distribution is discussed in relation to three controls: (1) increased ratios of octahedral to tetrahedral Ge in Na-rich, Ge-bearing melts and in high-pressure melts, (2) increased ratios of bivalent to quadrivalent Ge in highly reduced melts and (3) reduced admittance of Ge into the structurally ordered low microcline which crystallised in the low-temperature agpaitic magmas.

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As part of an on-going geochemical study, the distribution of germanium has been investigated in the rocks and minerals of the Ilímaussaq alkaline complex.

General properties of germanium

The igneous geochemistry of Ge is characterised by its occurrence at the level of 1–2 ppm, and by its entry into silicates as a result of the similarity in properties between Ge and the vastly more abundant Si (Hörmann 1970; Bernstein 1985).

With its high ionic potential, Ge readily forms tetrahedral complexes of $(GeO_4)^{4-}$ with mixed covalent–ionic bonding. These complexes are thought to replace $(SiO_4)^{4-}$ in silicate melts and minerals reflecting the fact that quadrivalent Ge and Si have similar covalent radii (Ge 1.22 Å, Si 1.17 Å; Cotton & Wilkinson 1966) and ionic radii (Ge 0.390 Å, Si 0.26 Å; Shannon 1976). In agreement with this, crystallographers have long recognised that germanates are isostructural with many silicates and many of these analogues have been synthesised experimentally.

Geochemists have generally assumed that Ge^{4+}, at trace element levels, follows Si^{4+} into silicate minerals and is thus tetrahedrally co-ordinated. The various anionic silicate groups found in minerals are demonstrably present in the local co-ordination of silicate glasses and melts (e.g. Hess 1980). It can thus be inferred that Ge, like Si, behaves as a network-forming cation in silicate melts.

In detail, when magmatic silicates crystallise it is found that Ge contents are higher in pyroxenes, amphiboles and olivines than in the tectosilicates feldspar or quartz where the three-dimensional silicate network is less amenable to distortion by the larger $(GeO_4)^{4-}$ tetrahedra.

Germanates with purely octahedral surroundings have also been reported, e.g. the perovskite-like $La_2Mg\,Ge^{VI}O_6$. Germanium dioxide has two polymorphs with differing anion co-ordination about the central cation: α-quartz-type GeO_2 with GeO_4 units, and rutile-type GeO_2 with GeO_6 units. Zeolitic germanates have GeO_4 tetrahedra and GeO_6 octahedra, e.g. $Na_3H(Ge^{VI}_4Ge^{IV}_3O_{16})\cdot nH_2O$ (Wittmann 1970).

The octahedral ionic radius of Ge^{4+} (0.53 Å), unlike the smaller radius of Si^{4+} (0.400 Å), should allow Ge^{4+} to follow Al^{3+} (0.535 Å), Ti^{4+} (0.605 Å), Fe^{3+} (0.645 Å) and Zr^{4+} (0.72 Å) into, e.g. Ti-rich minerals or the octahedral sites of mafic silicates. However, since optimal octahedral sites in the mafic silicates of igneous rocks are around 0.66–0.71 Å and significantly larger

than the germanium ion, the tendency to enter these sites will be reduced.

The electronegativity of Ge (2.01) is higher than those of Sn (1.96) and Si (1.90) and leads to the chalcophile character of Ge. Entry of Ge into sulphides, however, is more evident at low temperatures than in magmatic sulphides.

Compounds of divalent Ge are generally restricted to low-temperature reducing conditions and are not reliably established under natural conditions. Nevertheless, the possibility of high Ge^{2+}/Ge^{4+} ratios in the low-f_{O_2} agpaitic melts at Ilímaussaq is considered below.

During magmatic fractionation, early removal of olivine with a partition coefficient for Ge around 0.7 should lead to a slight increase in Ge contents (Capobianco & Watson 1982). However, with the subsequent fractionation of combinations of mafic silicates and feldspars, most magmatic series tend to maintain roughly constant Ge contents – around 1.4 ppm in basic rocks and 1.5 ppm in acid rocks (Bernstein 1985). Relatively high contents of Ge (x0–x00 ppm) in pegmatitic phases such as topaz, muscovite, spodumene, perthite and plagioclase suggest that Ge, at least locally, concentrates in highly fractionated Si-oversaturated magmas (Goldschmidt 1954; Bernstein 1985).

Germanium in alkaline rocks

No systematic studies have been made on the Ge contents of alkaline rocks. A compilation of recent data by the author suggests averages of around 1.3 ppm in nepheline syenites and 1.5 ppm in phonolites, i.e. levels close to those in other magmatic rocks. Similar values for alkaline rocks were reported by Novokhatskiy *et al.* (1968) and Schrön (1968).

In the Lovozero complex, Kola Peninsula, Russia, whole-rock analyses of Ge have not been reported but Ge has been detected by optical emission spectrometry in titanite, beryllite, sphalerite, lorenzenite and aenigmatite (Gerasimovsky *et al.* 1966).

In the Tezhsar complex of Armenia, Ge is present at around 1.6 ppm in nepheline syenites; it is concentrated in magnetite (5 ppm), titanite (10 ppm) and melanite (20 ppm), in accessory allanite (10–30 ppm), other REE minerals (30 ppm) and Ti-Nb minerals (30–100 ppm), and in secondary sodalite (30 ppm) (Meliksetyan 1971).

In the nepheline syenite pegmatites of Langesundsfjord in south Norway, optical emission spectrometric analyses revealed Ge in biotite (8.8 ppm), aegirine (10.4–12.3 ppm), oligoclase + nepheline (10.6 ppm) and perthite (22.7 ppm) (Hörmann 1963). From the same locality, older analyses indicate that orangite, a variety of zircon, contains 60 ppm Ge (Noddack & Noddack 1931) while the hydrothermal phases datolite with about 7 ppm and diaspore with about 70 ppm Ge (Goldschmidt 1954) also have relatively high contents of Ge.

Analytical method

Although Ge is rarely determined by X-ray fluorescence spectrometry, it is well within the capabilities of modern equipment. The following machine conditions were used: Philips PW1400 spectrometer, Mo tube, 80 kV, 30 mA, fine collimator, flow plus scintillation counter, LiF (200) crystal. The analysis was made for 400 seconds at the Ge$K\alpha$ peak and 400 seconds at the background at -0.46° 2θ, and was repeated four times for each sample. For many rock types there are no significantly interfering X-ray lines unless a tungsten carbide pot is used for grinding. However, in many Ilímaussaq rocks and minerals, interferences from Ta$L\beta_2$, W$L\beta_2$, W$L\beta_3$ and Zn$K\beta$ on Ge$K\alpha$ can be significant. They were monitored by determining interference factors on three synthetic mixtures made from pure SiO_2 and 100 ppm Ta, 100 ppm W and 1000 ppm Zn relative to Ta$L\beta_2$, W$L\beta_1$ and Zn$K\beta_1$, respectively, all with 100 seconds analytical time. Interference from the second-order tube line Mo$K\beta$ is potentially troublesome because it is matrix dependent. However, following the removal of Ta, W and Zn interferences, it was eliminated by computing Ge ppm values directly from peak/background ratios. Calibration was made against (1) a series of synthetic standards made from ultra-pure SiO_2, Fe_2O_3 and GeO_2 and (2) the international reference materials G-2 (1.14 ppm), W-1 (1.65 ppm) and Mica-Fe (3.2 ppm). Agreement between the two sets of standards was good. Under the above conditions, precision was close to ± 0.1 ppm and the detection limit was around 0.2 ppm. Accuracy can be judged from the following Ge ppm values on other reference materials (the values in brackets, where available, are from Govindaraju (1994), except for NIM-L which is from Halicz (1990)): GSP-1 1.2 (1.36), STM-1 1.35 (1.4), SY-2 1.3 (1.3), SY-3 1.35 (1.4), NIM-L 0.9 (0.89), NIM-S 0.5 (–), NIM-G 1.6 (–), ASK-1 1.5 (2), Mica-Mg 0.7 (0.55), FK-N 2.4 (2.5), MA-N 3.4 (3.5), AL-1 1.5 (1.4), ZGI-GNA 8.0 (–).

Minerals were separated by conventional methods

Table 1. The major rock types of the Ilímaussaq alkaline complex

Rock type	Texture	Essential minerals[*]	Minor minerals
Augite syenite	hypidiomorphic to xenomorphic granular, massive or layered, medium to coarse	alkali feldspar, hedenbergite, titanomagnetite, ferropargasite, olivine, biotite	ternary feldspar, apatite, pyrrhotite, nepheline
Pulaskite and foyaite	massive, medium to coarse, platy feldspars	alkali feldspar, nepheline, hedenbergite, fayalite, aegirine-augite to aegirine, katophorite	titanomagnetite, apatite, aenigmatite, biotite, fluorite, eudialyte
Sodalite foyaite	foyaitic, coarse	alkali feldspar, nepheline, sodalite, aegirine-augite to aegirine, katophorite, arfvedsonite	fayalite, hedenbergite, apatite, aenigmatite, titanomagnetite, eudialyte, rinkite, fluorite, biotite
Naujaite	poikilitic, coarse to pegmatitic	sodalite, alkali feldspar, nepheline, aegirine, arfvedsonite, eudialyte	aenigmatite, hedenbergite, aegirine-augite, fayalite, apatite, katophorite, rinkite, polylithionite, biotite, sphalerite, pectolite, villiaumite, fluorite, titanomagnetite
Kakortokite	laminated, layered, medium to coarse	alkali feldspar, nepheline, aegirine, arfvedsonite, eudialyte	sodalite, aenigmatite, magnetite, rinkite, fluorite, löllingite, sphalerite, galena
Lujavrite[†]	laminated, fine-grained; sometimes layered or massive, medium to coarse	microcline, albite, nepheline, sodalite, analcime, naujakasite, aegirine, arfvedsonite, eudialyte,	monazite, britholite, villiaumite, sphalerite, pectolite, steenstrupine, lovozerite, vitusite, polylithionite, ussingite, lueshite, neptunite
Alkali granite, quartz syenite	hypidiomorphic granular, medium to coarse	alkali feldspar, quartz, aegirine, arfvedsonite	aenigmatite, elpidite, zircon, ilmenite, pyrochlore, neptunite, fluorite, sphalerite

[*] Analcime and natrolite are secondary minerals in most rocks.
[†] There are several types of lujavrites. Three major groups may be distinguished: *aegirine or green lujavrite* with aegirine being the dominant mafic mineral; *arfvedsonite or black lujavrite*, fine grained, often laminated with arfvedsonite as the dominant mafic mineral; *medium- to coarse-grained lujavrite (M-C lujavrite)* with arfvedsonite as the dominant mafic mineral and generally showing foyaitic textures. *Naujakasite lujavrite* is a variety of arfvedsonite lujavrite containing naujakasite instead of nepheline and with steenstrupine instead of eudialyte.

of magnetic separation and heavy liquids. Corrections were made for impurities but proved to be insignificant in the present work.

Germanium in the Ilímaussaq complex

Ge contents in a number of Ilímaussaq rocks were reported in a preliminary study by Bailey *et al*. (1978), and these results have been confirmed and extended in the present work (Table 1). An outline of the geology and rock types at Ilímaussaq, together with localities referred to here, is given by Sørensen (2001, this volume) and can be supplemented by the references therein.

Overall, median Ge contents decrease slightly through the sequence of rocks in the Ilímaussaq complex (Table 1) from around 1.8 ppm in augite syenite to 1.6 ppm in pulaskite + foyaite, 1.65 ppm in sodalite foyaite + naujaite and 1.7 ppm in bulk kakortokite to 0.9 ppm in aegirine lujavrite; there is a partial recovery in arfvedsonite lujavrite (1.6 ppm) and medium- to coarse-grained lujavrite (1.6 ppm). However, in a wider survey of 21 smaller samples of medium- to coarse-grained lujavrite from drill cores, Ge contents were generally lower, ranging from 0.2 to 2.2 ppm with a median of 1.4 ppm. Among the Si-oversaturated rocks, levels in quartz syenite (1.8 ppm) and alkali granite (1.7 ppm) are close to those in augite syenite.

Samples of dykes and sills that are thought to represent Ilímaussaq liquids (Bailey *et al*. 2001, this volume), although few in number, also show a decreasing trend, from 1.9 to 1.6 ppm Ge.

The gentle trends found through the sequence of rock types in the complex can hide significant variations: from 1.3 to 2.4 ppm in sodalite foyaite, and from 1.2 ppm in a white kakortokite to 3.7 ppm in a black kakortokite. Given that Ge is one of the most geochemically monotonous elements in igneous rocks, its wide range of contents at Ilímaussaq is particularly striking.

There is a clear correlation with Fe in many rock types, particularly the kakortokites where, as total Fe decreases from 29 to 4 wt%, Ge decreases from 3.7 to 1.2 ppm. This reflects a trend from cumulates rich in arfvedsonite and aegirine (black kakortokites) to cumulates rich in feldspar, nepheline and zeolites (white kakortokites).

Along with the marked Ge–Fe correlation in individual rock types at Ilímaussaq, there is a trend towards decreasing Ge contents at any given Fe content. Thus, at 9% Fe, contents of Ge decrease from around 1.9 ppm in augite syenite through 1.7 ppm in sodalite foyaite + naujaite to 1.6 ppm in kakortokites and the following lujavrites.

The distribution of Ge among minerals co-existing in individual samples is given in Table 2, and can be supplemented by data on minerals scattered through the various rock types.

The main carriers of Ge at Ilímaussaq are the amphiboles: katophorite in pulaskite (4.5–5.3 ppm), and arfvedsonite in sodalite foyaite (4.1–5.2 ppm), naujaite

Table 1 (continued)

Mineral	Formula	Reference
Cuprite	Cu_2O	López-Soler et al. (1975)
Cuprostibite	$Cu_2(Sb,Tl)$	Sørensen et al. (1969)
Dahllite, see carbonate-hydroxylapatite		
Diaspore	$AlO(OH)$	Ussing (1894)
Digenite	$Cu_{1.8}S$	López-Soler et al. (1975)
Djerfisherite	$K_6(Na,Li)(Fe,Cu,Ni)_{24}S_{26}Cl$	Karup-Møller (1978b)
Djurleite *	$Cu_{1.96}S$	Karup-Møller et al. (1978)
Dorfmanite	$Na_2(PO_3OH)\cdot 2H_2O$	Petersen et al. (1993)
Dyscrasite	Ag_3Sb	López-Soler et al. (1975)
Elpidite	$Na_2ZrSi_6O_{15}\cdot 3H_2O$	Ussing (1912)
Ephesite	$NaLiAl_2(Si_2Al_2)O_{10}(OH)_2$	Semenov (2001)
Epididymite	$NaBeSi_3O_7(OH)$	Hamilton (1964)
Epidote	$Ca_2FeAl_2(Si_2O_7)(SiO_4)(O,OH)_2$	Flink (1898)
Epistolite	$Na_2TiNb_2(Si_2O_7)_2(O,F)_4\cdot 5H_2O$	Bøggild (1899)
Erikite ‡		Bøggild (1903), Pekov et al. (1997a)
Eudialyte	$Na_{15}Ca_6Fe_3Zr_3Si(Si_{25}O_{73})(O,OH,H_2O)_3(Cl,OH)_2$	Stromeyer (1819)
Eudidymite	$Na_2Be_2Si_6O_{15}\cdot H_2O$	Semenov & Sørensen (1966)
Evenkite * †	$C_{24}H_5$	
Famatinite	Cu_3SbS_4	Karup-Møller (1974)
Fayalite	Fe_2SiO_4	Ussing (1912)
Ferrosalite	$Ca_3Fe_2Mg(Si_2O_6)_3$	Larsen (1976)
Ferropargasite	$NaCa_2(Fe,Mg,Al)_5(Si_6Al_2)O_{22}(OH)_2$	Larsen (1976)
Fersmite	$(Ca,Ce,Na)(Nb,Ta,Ti)_2(O,OH,F)_6$	Petersen et al. (1998)
Fluorite	CaF_2	1809 (Giesecke)‡‡
Galena	PbS	1809 (Giesecke)‡‡
Garnet (group)		Flink (1898)
Gelbertrandite * ‡		Semenov (1969)
Genthelvite	$Be_3Zn_4(SiO_4)_3S$	Bollingberg & Petersen (1967)
Gerasimovskite	$(Mn,Ca)(Nb,Ti)_5O_{12}\cdot 9H_2O(?)$	Semenov et al. (1967a)
Gmelinite	$Na_4(Al_4Si_8)O_{24}\cdot 11H_2O$	Karup-Møller (1976)
Goethite (limonite)	$FeO(OH)$	1806 (Giesecke)‡‡
Gold	Au	Davison (1989), Bohse & Frederiksen (2001)
Gonnardite (formerly tetranatrolite)	$(Na,K)_2(Si,Al)_5O_{10}\cdot 2H_2O$	Grice (2001)
Gudmundite	$FeSbS$	Oen & Sørensen (1964)
Halite	$NaCl$	Sobolev et al. (1970)
Halloysite	$Al_2Si_2O_5(OH)_4$	Semenov (1969)
Hastingsite	$NaCa_2(Fe,Mg)_5(Si_6Al_2)O_{22}(OH,Cl)_2$	Larsen (1976)
Hedenbergite	$Ca(Fe,Mg)Si_2O_6$	Semenov (1969)
Helvite	$Be_3Mn_4(SiO_4)_3S$	Johnsen & Bohse (1981)
Hematite	Fe_2O_3	Ussing (1894)
Hemimorphite	$Zn_4Si_2O_7(OH)_2\cdot H_2O$	Sørensen (1962)
Herschelite	$(Na,Ca,K)(AlSi_2)O_6\cdot 3H_2O$	Karup-Møller (1976)
Hisingerite	$Fe_2Si_2O_5(OH)_4\cdot 2H_2O$	Semenov (1969)
Hiortdahlite	$Na_4Ca_8Zr_2(Nb,Mn,Ti,Fe,Mg,Al)_2(Si_2O_7)_4O_3F_5$	Larsen & Steenfelt (1974), Robles et al. (2001)
Hydrargillite (gibbsite)	$Al(OH)_3$	Semenov (1969)
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	Karup-Møller (1975)
Hydronephelite ‡		Ussing (1894)
Ilimaussite	$Na_4Ba_2CeFeNb_2Si_8O_{28}\cdot 5H_2O$	Semenov et al. (1968)
Ilmenite	$FeTiO_3$	Ussing (1912)
Ilvaite	$CaFe^{3+}(Fe^{2+})_2O(Si_2O_7)(OH)$	Lorenzen (1881)
Joaquinite-(Ce)	$NaBa_2FeTi_2Ce_2(SiO_3)_8O_2(OH)\cdot H_2O$	Semenov (1969)
Katophorite	$(Na,Ca)_3(Mg,Fe,Al)_5(Si_7Al)O_{22}(F,OH)_2$	Ussing (1912)
Karupmøllerite-Ca †		Name accepted by IMA 2001
Kvanefjeldite	$Na_4(Ca,Mn)Si_6O_{14}(OH)_2$	Johnsen et al. (1983), Petersen et al. (1984)

(4.3–6.0 ppm), kakortokite (3.7–4.4 ppm), aegirine lujavrite I (3.7–4.7 ppm), aegirine lujavrite II (2.4 ppm), arfvedsonite lujavrite (6.2–6.3 ppm), medium- to coarse-grained lujavrite (3.9–4.5 ppm), pegmatites (3.7–5.0 ppm) and veins (4.4–6.2 ppm).

Slightly lower levels occur in pyroxenes: heden-bergite in augite syenite (3.6 ppm), aegirine-augite in pulaskite (3.7–4.0 ppm), and aegirines in sodalite foyaite (3.8–4.1 ppm), naujaite (3.7–4.3 ppm), kakortokite (3.7 ppm), aegirine lujavrite I (2.5–3.4 ppm), aegirine lujavrite II (2.9–3.6 ppm), pegmatites (2.9–3.3 ppm) and veins (3.2–4.3 ppm).

There are no well-defined trends in Ge contents for these two minerals as the Ilímaussaq system evolves, not even at the stage of pegmatites and veins. Cumulus and intercumulus varieties also show no clear differences.

In contrast, Ge contents in microcline show an ir-regular decrease from augite syenite (1.4 ppm) through sodalite foyaite (0.4 ppm), naujaite (0.5–0.8 ppm), ka-kortokite (0.8 ppm), aegirine lujavrite I (0.3–0.4 ppm), aegirine lujavrite II (< 0.2 ppm) and medium- to coarse-grained lujavrite (0.2–0.3 ppm). Among pegmatites, the Ge content of microcline decreases from a naujaite pegmatite (1.6 ppm) to the border pegmatites adja-cent to the kakortokites (0.6 ppm) and on Kvanefjeld (0.7 ppm). The decreasing contents of Ge appear to be linked to the degree of structural order in the mi-crocline, from microcline microperthite in the augite syenite and early nepheline syenites to low micro-cline in the late nepheline syenites (Table 2). This relationship is considered more fully in the discus-sion below.

At the magmatic stage, other leucosilicates also gen-erally have low contents of Ge: nepheline (< 0.2–1.3 ppm), sodalite (0.3–0.5 ppm) and the zeolites analcime and natrolite (< 0.2–0.3 ppm). In veins, Ge contents are even lower in sodalite (< 0.2 ppm) and albite (< 0.2 ppm), and are barely higher in analcime (< 0.2–0.2 ppm), tugtupite (0.2 ppm), natrolite (< 0.2–0.5 ppm), ussingite (0.2–0.5 ppm) and chkalovite (0.5 ppm). In the magmatic rocks, the crystallisation sequence for leucocratic phases both within and between the various rock types is early microcline and nepheline

Fig. 1. Distribution of Ge in co-existing mafic silicates and K-feldspars in the Ilímaussaq complex and other igneous rocks. The character of the mafic silicate is distinguished by different symbols. Data for pyroxene–sanidine pairs in rhyolites from Ewart & Griffin (1994) and for biotite–K-feldspar pairs in granites from Hörmann (1963) and Schrön (1968). Note the low Ge contents in microclines from the Ilímaussaq agpaitic nepheline syenites.
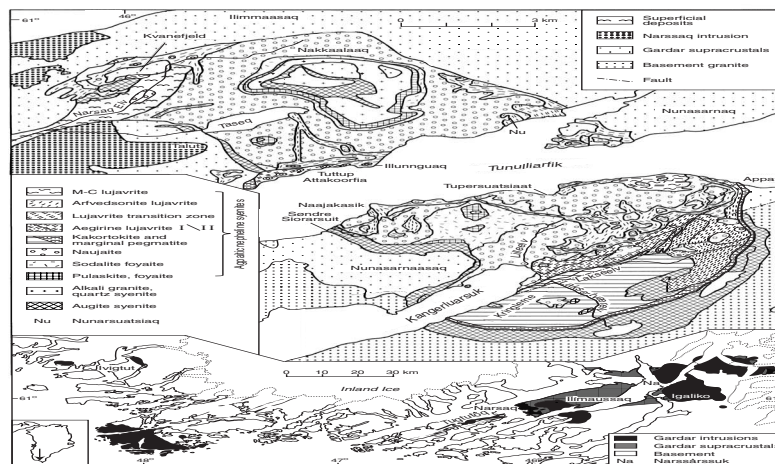
± sodalite but late analcime and natrolite, and it is clear that this sequence is characterised by generally decreasing contents of Ge.

Of the remaining rock-forming minerals, Ge contents in eudialyte (1.3–1.9 ppm) and steenstrupine (0.7–0.9 ppm) were determined with great difficulty because of large interferences but seem unremarkable.

To date, Ge contents greater than 10 ppm have been detected only in two minerals. Aenigmatite from naujaite pegmatites contains 10.2–10.7 ppm Ge, recalling the high Ge level of 22.1 ppm reported in phenocrystal aenigmatite from a peralkaline rhyolite at Mayor Island, New Zealand (Ewart & Griffin 1994). Around 50 ppm Ge was reported for aenigmatite from alkali pegmatites (Vlasov 1966), presumably from Lovozero, Russia.

Sphalerite from an albite-steenstrupine vein at Ilímaussaq contains 42 ppm Ge but a second sphalerite from a different vein only contains 7.8 ppm Ge, and the rare antimonide cuprostibite has 5.0 ppm. Thus the chalcophile tendencies of Ge appear subdued in the Ilímaussaq complex.

Judged from mineral analyses, especially the relatively low levels in sphalerite which is only of local occurrence, it seems likely that the decreasing trend of Ge contents in the Ilímaussaq magmas continues into late pegmatites and veins.

Overall, the outstanding feature of the geochemistry of Ge at Ilímaussaq is the change in the mineralogical distribution of Ge between the augite syenite and the agpaitic nepheline syenites. The distribution of Ge in augite syenite is consistent with that established at other igneous localities: pyroxene > olivine > feldspar (Harris 1954) and the minerals show comparable absolute contents. In the agpaitic nepheline syenites, the mineralogical preference is generally: aen-

igmatite > arfvedsonite > aegirine > eudialyte > microcline = nepheline > sodalite > zeolites. Partition coefficients for Ge between minerals and magma, though only roughly estimated, are highest in aenigmatite (6), arfvedsonite (3) and aegirine (2) and distinctly lower in K-feldspar (0.5 falling to 0.1) and other tectosilicates.

Most significantly, the Ge contents of K-feldspars in the agpaitic nepheline syenites of Ilímaussaq are exceptionally low and fall from about 0.8 to 0.2 ppm during magmatic evolution (Fig. 1). These levels contrast sharply with contents in K-feldspars in the augite syenite at Ilímaussaq (1.4 ppm), and in granites (0.9–3.8 ppm) and granitic pegmatites (2.1–29.2 ppm) from various localities (Hörmann 1963; Novokhatskiy *et al.* 1968; Schrön 1968; Bernstein 1985; author's unpublished data). Contents in other Ilímaussaq tectosilicates (nepheline, sodalite, analcime and natrolite) can also fall to < 0.2 ppm.

In terms of partitioning between co-existing minerals, the ratio of Ge in mafic silicate to K-feldspar is *c.* 1–5 in normal igneous rocks but 5–20 in the Ilímaussaq agpaitic rocks (Fig. 1).

Discussion

The paucity of Ge in Ilímaussaq tectosilicates and consequently its unusual distribution between co-existing silicates can be explained by several mechanisms.

Co-ordination of Ge

Firstly, studies on sodium germanate glasses indicate that the co-ordination of Ge changes with increasing

contents of sodium and with increasing pressure. The similarity in behaviour of Ge and Si in glasses is far from perfect, since alkali germanate glasses show maxima and minima in physical properties such as density, viscosity and heat of solution at around 20 mol.% Na_2O and this behaviour is absent in alkali silicate glasses. Liquid and vitreous GeO_2 forms a disordered three-dimensional network made up of GeO_4 tetrahedra joined at their corners. It has been argued that, with addition of Na_2O, the tetrahedral units are converted into octahedral GeO_6 units. For each oxygen added to GeO_2 as Na_2O, one octahedron is produced without, however, formation of non-bridging oxygens. Studies by X-ray diffraction (Kamiya & Sakka 1979), extended X-ray absorption spectroscopy (Lapeyre *et al.* 1983) and neutron scattering (Ueno *et al.* 1983) suggest that the fraction of octahedral Ge atoms increases linearly with increasing Na_2O content and reaches a maximum in the vicinity of mol. fraction Na_2O (x) = 0.20. During the conversion of GeO_4 to complex $(GeO_6)^{2-}$ ions, charge neutrality would be maintained by addition of $2Na^+$. The increased packing efficiency of the GeO_6 units could explain the observed maximum in density around x = 0.20.

High-temperature X-ray diffraction suggests that at x = 0.20, glasses and melts have a structure similar to $Na_2Ge_4O_9$ crystals which can crystallise in metastable form and which contain both GeO_6 octahedra and GeO_4 tetrahedra (Kamiya *et al.* 1988).

However, Henderson & Fleet (1991) consider that these various spectral studies have been misinterpreted and that the evidence simply indicates that a lengthening of the Ge–O bonds occurs as Na_2O is added to the glass. They propose that bond lengthening is not due to GeO_6 formation but to distortions of the tetrahedra which occur when small three-membered GeO_4 rings are formed.

Hussin *et al.* (1998) admit that the correct structural model for alkali germanate glasses is still unknown, and that both the above models may prove to have some validity. Their own nuclear magnetic resonance structural analysis revealed different chemical shifts for oxygen in GeO_4 and GeO_6 units in quartz-type and rutile-type GeO_2, respectively. Furthermore, they found that in sodium germanate glasses at 10 mol.% Na_2O some fraction of the germanium is in sixfold co-ordination whereas at 18.2 mol.% Na_2O the co-ordination is predominantly fourfold.

Pressure is potentially an additional factor, since there is a gradual change from fourfold to sixfold Ge co-ordination in GeO_2 and Na_2O–GeO_2 glasses (Itié *et*

al. 1989) and in $MgGeO_3$ enstatite and $CaGeO_3$ wollastonite (Andrault *et al.* 1992) with increasing pressure. Raman spectra on high-temperature glasses and liquids of $Na_2Ge_2O_5 \cdot H_2O$ composition indicate that the proportion of Ge^{VI} relative to Ge^{IV} increases several fold with pressure up to 22 kbar, from near 0% to > 50% (Farber & Williams 1992). This suggests that the change from ambient pressure to 1 kbar, the pressure inferred for the Ilímaussaq system 3–4 km below the contemporary surface (see Sørensen 2001, this volume), would only increase the proportion of Ge^{VI} by a few percent relative. Such a small increase is not consistent with the pronounced changes in Ge distribution at Ilímaussaq, e.g. Ge contents of K-feldspar varying from 1.4 to < 0.2 ppm. Furthermore, it fails to explain why the minerals of other shallow-level intrusions reveal a markedly different Ge distribution from those in the Ilímaussaq complex.

There is, of course, a considerable step from simple sodium germanate glasses to natural and highly complex silicate melts where Ge occurs at the 1–2 ppm level. We can only speculate, therefore, that if the high Ge^{VI}/Ge^{IV} ratios of Na-bearing glasses, i.e. melts, persist during the transition to the crystalline state, then minerals favouring Ge^{VI} will tend to have higher Ge contents than normal whereas minerals favouring Ge^{IV} will tend to have lower. This appears consistent with the low contents of Ge in Ilímaussaq tectosilicates where only Ge^{IV} is able to enter.

The question then arises whether there is evidence to show that Ge^{VI} concentrates in minerals along with octahedrally co-ordinated Al, Ti, Fe^{3+} and Zr. Larsen (1976) has demonstrated that, as the Ilímaussaq system becomes more agpaitic, these elements increasingly enter octahedral sites in pyroxenes, occurring as the components $NaFe^{3+}Si_2O_6$, $NaAlSi_2O_6$ and $Na(Ti,Zr)AlSiO_6$. However, only Fe^{3+} has a size close to optimum for the M1 site in pyroxenes and it can be estimated that partition coefficients between pyroxene and melt decrease rapidly from roughly 5 (Fe^{3+}) to 2 (Zr), 1 (Ti) and 0.1 (Al). Ignoring their different valencies, octahedral Ge^{4+} (0.53 Å) with a similar size to octahedral Al^{3+} (0.535 Å) would also be expected to show only minor partitioning into the M1 sites of pyroxenes.

Among the Ilímaussaq silicates, the Ti mineral aenigmatite has the highest content of Ge – slightly above 10 ppm. Significantly, one of the octahedral sites in aenigmatite is distinctly smaller than the remaining six (nearest neighbour distance of 1.98 Å versus 2.10–2.17 Å) (Cannillo *et al.* 1971). This single site favours entry of a cation with an ionic radius of 0.60 Å ex-

plaining the high occupancy of Ti^{4+} (0.605 Å) and presumably of Ge^{4+} (0.53 Å). Aenigmatite, however, is never more than a minor to accessory phase at Ilímaussaq and is unlikely to influence the entry of Ge into the rock-forming minerals.

Valency of Ge

The occurrence at Ilímaussaq of melts with low oxygen fugacities (see below) may have converted some of the Ge from a quadrivalent to bivalent state. Among the rock-forming minerals, Ge shows preferential entry into Fe^{2+}-rich arfvedsonite rather than Fe^{3+}-rich aegirine. This might be explained by the details of the two silicate structures, but it may also point to the presence of Ge in bivalent rather than quadrivalent form. In octahedral co-ordination, Ge^{2+} has a formal ionic radius of 0.73 Å, distinctly higher than the ionic radius for Ge^{4+} (0.53 Å), and might be expected to substitute for Fe^{2+} (0.78 Å). Furthermore, a magma with a high Ge^{2+}/Ge^{4+} ratio will contain fewer $(GeO_4)^{4-}$ ions and this will lead to reduced substitution of Si in tetrahedral sites. This reduced substitution would be most visible among the leucosilicates where tetrahedral sites are the only possible point of entry for Ge.

The highly reduced character of the agpaitic melts at Ilímaussaq has been repeatedly emphasised. At the magmatic stage, it is seen by the displacement of the FMQ buffer curve to low values of oxygen fugacity, by the presence of ferri-aenigmatite, arfvedsonite (Larsen 1977) and native lead (Karup-Møller 1978), and by the presence of CH_4 or H_2 or both in fluid inclusions (Konnerup-Madsen et al. 1981).

Experimental work on the valency of Ge in reduced magmas should throw light on these ideas. Here, one can only note that the chemically similar element below Ge in Group IVA is Sn and recent work has demonstrated that Sn^{2+}/Sn^{4+} ratios in haplogranitic melts rise sharply under more reducing conditions (Linnen et al. 1996). However, Sn shows a much greater tendency to occur in the bivalent state than Ge, and the quadrivalent compounds of Ge are more stable than its bivalent compounds (Rochow & Abel 1975). Furthermore, Ge^{2+} is a distinctly lone-electron-pair element and requires an irregular co-ordination polyhedron (E. Makovicky, personal communication 1999).

It also seems likely that, if Ge^{2+} were actually to substitute for Fe^{2+} in octahedral sites of arfvedsonite, more substitution would be expected than is observed. Ge contents in arfvedsonite are similar to those in inosilicates at many localities and are not dramatically higher than those in Fe^{2+}-poor aegirine.

Feldspar structure

Variations in the structure of the Ilímaussaq K-feldspars may have played a role in the partitioning of Ge. As a broad generalisation, the ability of crystals to take in non-stoichiometric cations increases under rapid, structurally disordered or high-temperature crystallisation.

Feldspars show particularly complex relations. Most igneous feldspars crystallise with disordered Al and Si atoms but, on cooling or during direct crystallisation at lower temperatures, the Si and Al ordering increases. In high sanidine, all T–O distances between the tetrahedral cation and the oxygen anion statistically lie around 1.642 Å; in intermediate microcline, on average, two T–O distances are relatively large (1.694 and 1.642 Å) and two are small (1.618 and 1.616 Å); in low microcline, on average, a single T–O distance is large (1.741 Å) and the other three are small (around 1.613 Å) (Smith 1977; Blasi et al. 1984). Using a radius of 1.38 Å for fourfold O^{2-} (Shannon 1976), the optimal ionic radii for the tetrahedral cations are 0.26 Å in high sanidine; 0.31, 0.26 and 0.24 Å in intermediate microcline; and 0.36 and 0.23 Å in low microcline. Si^{4+} (0.26 Å) will tend to prefer the smaller sites whereas Al^{3+} (0.39 Å) will tend to prefer the largest site in low microcline. Hence the increased ordering.

It is expected that during partitioning into these different types of K-feldspar, the Ge^{4+} ion will be introduced randomly into all four tetrahedral sites in high sanidine, but will have more difficulty in entering tetrahedral sites in high microcline and even greater difficulty in entering any tetrahedral sites in low microcline. This is because Ge^{4+} (0.39 Å) cannot easily follow Si^{4+} into the three smaller sites of low microcline as a result of its much larger size and cannot easily follow Al^{3+} into the largest site as a result of charge balancing problems. The content of Al in these three feldspars will be constant because of stoichiometric requirements but the content of Ge should decrease towards low microcline because of the reduced number of suitable tetrahedral sites.

Low microcline is rare in nature but is known from low-temperature agpaitic nepheline syenites where it shows characteristic 'chessboard' or 'tiled' twinning. At Ilímaussaq, it occurs as euhedral to subhedral tablets or laths, and these may have crystallised directly with high or maximum triclinicity from the magma at

< 400°C (Brøgger 1890; Ussing 1898; Vlasov *et al*. 1959; Sørensen 1962; Borutskii & Semenov 1969; Ferguson 1970; Smith & McLaren 1983). These studies also demonstrated that the earlier, higher temperature K-feldspars at Ilímaussaq are microcline microperthites, moderately ordered in augite syenite but highly ordered in the nepheline syenites.

Based solely on microscope observations, the two types of feldspar at Ilímaussaq are indicated in Table 2. The microcline perthites from the agpaitic nepheline syenites which, according to the detailed studies noted above, are highly ordered have lower Ge contents than K-feldspars from 'normal' granitic and rhyolitic rocks. Microclines with even lower Ge contents (0.3 ppm or less) are judged to be low microclines where none of the tetrahedral sites is suitable for Ge.

On present evidence, the low Ge contents in the Ilímaussaq microclines, and perhaps in the other leucosilicates, appear to be linked to the high degree of ordering attained during crystallisation under exceptionally low-temperature conditions. The unusual distribution of Ge may thus be yet another expression of crystallisation in an agpaitic system.

Conclusions

1. Germanium contents in Ilímaussaq rocks and magmas (dykes, sills) decrease from about 1.8 to 1.5 ppm, and probably fall to even lower levels in late pegmatites and veins. In the agpaitic rocks, the bulk of Ge is held in arfvedsonite (2.4–6.3 ppm) and aegirine (2.5–4.3 ppm) with lower contents in eudialyte (1.3–1.9 ppm), microcline (< 0.2–0.8 ppm), nepheline (< 0.2–1.3 ppm), sodalite (0.3–0.5 ppm), analcime and natrolite (< 0.2–0.3 ppm). The highest contents are reported from aenigmatite (10.2–10.7 ppm) in pegmatites and sphalerite (7.8–42 ppm) in veins.

2. It is significant that mafic silicates have normal contents of Ge, whereas microcline has low and decreasing contents – from 0.8 to < 0.2 ppm.

3. Conversion of some Ge from fourfold to sixfold co-ordination is likely in Na-rich melts, but the size of Ge^{4+} ions in sixfold co-ordination is too small to significantly promote entry into the octahedral sites of Ilímaussaq mafic silicates.

4. Reduction of some Ge^{4+} to Ge^{2+} is conceivable in the low-fo_2 magmas at Ilímaussaq. It should promote the entry of Ge^{2+} into Fe^{2+}-rich minerals such as arfvedsonite but this is not observed.

5. The decreasing Ge contents in microclines appear to be linked to crystallisation over a wide temperature range. Early microcline microperthites are moderately ordered but give way to highly ordered microcline microperthites and then to low microclines which crystallised at exceptionally low magmatic temperatures. It is argued that, in these low microclines, Ge^{4+} has difficulty in entering any of the highly ordered tetrahedral sites.

References

Andrault, D., Madon, M., Itié, J.P. & Fontaine, A. 1992: Compression and coordination changes in pyroxenoids: an EXAFS study of $MgGeO_3$ enstatite and $CaGeO_3$ wollastonite. Physics and Chemistry of Minerals **18**, 506–513.

Bailey, J., Gwozdz, R., Rose-Hansen, J. & Sørensen, H. 1978: Preliminary geochemical work on the Ilímaussaq alkaline intrusion, South Greenland. Rapport Grønlands Geologiske Undersøgelse **90**, 75–79.

Bailey, J.C., Gwozdz, R., Rose-Hansen, J. & Sørensen, H. 2001: Geochemical overview of the Ilímaussaq alkaline complex, South Greenland. In: Sørensen, H. (ed.): The Ilímaussaq alkaline complex, South Greenland: status of mineralogical research with new results. Geology of Greenland Survey Bulletin **190**, 35–53 (this volume).

Bernstein, L.R. 1985: Germanium geochemistry and mineralogy. Geochimica et Cosmochimica Acta **49**, 2409–2422.

Blasi, A., Brajkovic, A., De Pol Blasi, C., Foord, E.E., Martin, R.F. & Zanazzi, P.F. 1984: Structure refinement and genetic aspects of a microcline overgrowth on amazonite from Pikes Peak batholith, Colorado, U.S.A. Bulletin de Minéralogie **107**, 411–422.

Borutskii, B.E. & Semenov, E.I. 1969: Feldspars from the Ilímaussaq alkaline massif. Trudy Mineralogicheskogo Muzeya im. A.E. Fersman **19**, 3–11 (in Russian).

Brøgger, W.C. 1890: Die Mineralien der Syenitpegmatitgänge der südnorwegischen Augit- und Nephelinsyenite. Zeitschrift für Krystallographie und Mineralogie **16**, 663 pp.

Cannillo, E., Mazzi, F., Fang, J.H., Robinson, P.D. & Ohya, Y. 1971: The crystal structure of aenigmatite. American Mineralogist **56**, 427–446.

Capobianco, C.J. & Watson, E.B. 1982: Olivine/silicate melt partitioning of germanium: an example of a nearly constant partition coefficient. Geochimica et Cosmochimica Acta **46**, 235–240.

Cotton, F.A. & Wilkinson, G. 1966: Advanced inorganic chemistry, 530 pp. New York: Wiley.

Ewart, A. & Griffin, W.L. 1994: Application of proton-microprobe data to trace-element partitioning in volcanic rocks. Chemical Geology **117**, 251–284.

Farber, D.L. & Williams, Q. 1992: Pressure-induced coordination changes in alkali-germanate melts: an in situ spectroscopic investigation. Science **256**, 1427–1430.

Ferguson, J. 1970: The significance of the kakortokite in the evolution of the Ilímaussaq intrusion, South Greenland. Bulletin Grønlands Geologiske Undersøgelse **89**, 193 pp. (also Meddelelser om Grønland **190**(1)).

Gerasimovsky, V.I., Volkov, V.P., Kogarko, L.N., Polyakov, A.I., Saprykina, T.V. & Balashov, Yu.A. 1966: The geochemistry of the Lovozero alkaline massif. Moscow: Nauka (in Russian). (Translation: Brown, D.A. 1968: 2 vols., 224 pp. and 369 pp. Canberra: Australian National University Press and Toronto: University of Toronto Press.)

Goldschmidt, V.M. 1954: Geochemistry, 730 pp. London: Oxford University Press.

Govindaraju, K. 1994: 1994 compilation of working values and sample description for 383 geostandards. Geostandards Newsletter **18**, Special Issue, 158 pp.

Halicz, L. 1990: Germanium contents of selected international geostandards by hydride generation and ICP-AES. Geostandards Newsletter **14**, 459–460.

Harris, P.G. 1954: The distribution of germanium among coexisting phases of partly glassy rocks. Geochimica et Cosmochimica Acta **5**, 185–195.

Henderson, G.S. & Fleet, M.E. 1991: The structure of glasses along the Na_2O–GeO_2 join. Journal of Non-Crystalline Solids **134**, 259–269.

Hess, P.C. 1980: Polymerization model for silicate melts. In: Hargraves, R.B. (ed.): Physics of magmatic processes, 3–48. Princeton: Princeton University Press.

Hörmann, P.K. 1963: Zur Geochemie des Germaniums. Geochimica et Cosmochimica Acta **27**, 861–876.

Hörmann, P.K. 1970: Germanium. B–M, O. In: Wedepohl, K.H. (ed.): Handbook of geochemistry **II/3**, 61 pp. Berlin: Springer Verlag.

Hussin, R., Holland, D. & Dupree, R. 1998: Does six-coordinate germanium exist in Na_2O–GeO_2 glasses? Oxygen-17 nuclear magnetic resonance measurements. Journal of Non-Crystalline Solids **232–234**, 440–445.

Itié, J.P., Polan, A., Calas, G., Petiau, J., Fontaine, A. & Tolentino, H. 1989: Pressure-induced coordination changes in crystalline and vitreous GeO_2. Physical Review Letters **63**, 398–401.

Kamiya, K. & Sakka, S. 1979: X-ray diffraction study of Na_2O–GeO_2 glasses and coordination number of germanium. Physics and Chemistry of Glasses **20**, 60–64.

Kamiya, K., Yoko, T., Hashimoto, Y. & Sakka, S. 1988: Crystallization behavior of $xNa_2O\cdot(1-x)GeO_2$ glasses and melts with x of 0 to 0.30. Materials Research Bulletin **23**, 363–369.

Karup-Møller, S. 1978: The ore minerals of the Ilímaussaq intrusion: their mode of occurrence and their conditions of formation. Bulletin Grønlands Geologiske Undersøgelse **127**, 51 pp.

Konnerup-Madsen, J., Rose-Hansen, J. & Larsen, E. 1981: Hydrocarbon gases associated with alkaline igneous activity: evidence from compositions of fluid inclusions. In: Bailey, J.C., Larsen, L.M. & Sørensen, H. (eds): The Ilímaussaq intrusion, South Greenland. A progress report on geology, mineralogy, geochemistry and economic geology. Rapport Grønlands Geologiske Undersøgelse **103**, 99–108.

Lapeyre, C., Petiau, J., Calas, G., Gauthier, F. & Gombert, J. 1983: Ordre local autour du germanium dans les verres du système SiO_2–GeO_2–B_2O_3–Na_2O: étude par spectrométrie d'absorption X. Bulletin de Minéralogie **106**, 77–85.

Larsen, L.M. 1976: Clinopyroxenes and coexisting mafic minerals from the alkaline Ilímaussaq intrusion, South Greenland. Journal of Petrology **17**, 258–290.

Larsen, L.M. 1977: Aenigmatites from the Ilímaussaq intrusion, South Greenland: Chemistry and petrological implications. Lithos **10**, 257–270.

Linnen, R.L., Pichavant, M. & Holtz, F. 1996: The combined effects of fo_2 and melt composition on SnO_2 solubility and tin diffusivity in haplogranitic melts. Geochimica et Cosmochimica Acta **60**, 4965–4976.

Meliksetyan, B.M. 1971: Mineralogy, geochemistry and petrological character of Tezhsar alkali complex. In: Petrology of intrusive complexes of the most important ore deposits in the area of Armenian SSR, 117–290. Yerevan: Akademii Nauk Armyanskoy SSR (in Russian).

Noddack, I. & Noddack, W. 1931: Zur Geochemie des Rheniums. Zeitschrift für Physikalische Chemie **154**, 207–244.

Novokhatskiy, I.P., Kalinin, S.K. & Zamyatina, G.M. 1968: The germanium content of igneous and altered rocks of Kazakhstan. Izvestiya Akademii Nauk Kazakhskoi SSR, Seriya Geologicheskaya **25**(1), 81–85 (Geochemistry International **4**, 1192–1196, 1967).

Rochow, E.G. & Abel, E.W. 1975: The chemistry of germanium, tin and lead, 233 pp. New York: Pergamon Press.

Schrön, W. 1968: Ein Beitrag zur Geochemie des Germaniums. Chemie der Erde **27**, 193–251.

Shannon, R.D. 1976: Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica **A32**, 751–767.

Smith, J.V. 1977: Feldspar minerals **1**, 627 pp. Berlin: Springer Verlag.

Smith, K.L. & McLaren, A.C. 1983: TEM investigation of a microcline from a nepheline syenite. Physics and Chemistry of Minerals **10**, 69–76.

Sørensen, H. 1962: On the occurrence of steenstrupine in the Ilímaussaq massif, Southwest Greenland. Bulletin Grønlands Geologiske Undersøgelse **32**, 251 pp. (also Meddelelser om Grønland **167**(1)).

Sørensen, H. 2001: Brief introduction to the geology of the Ilí-

maussaq alkaline complex, South Greenland, and its exploration history. In: Sørensen, H. (ed.): The Ilímaussaq alkaline complex, South Greenland: status of mineralogical research with new results. Geology of Greenland Survey Bulletin **190**, 7–23 (this volume).

Ueno, M., Misawa, M. & Suzuki, K. 1983: On the change in coordination of Ge atoms in Na_2O–GeO_2 glasses. Physica (Utrecht) **120B**, 347–351.

Ussing, N.V. 1898: Mineralogisk-petrografiske Undersøgelser af grønlandske Nefelinsyeniter og beslægtede Bjærgarter. Første Del: Alkalifeldspaterne. Meddelelser om Grønland **14**, 1–106.

Vlasov, K.A. 1966: Geochemistry and mineralogy of rare elements and genetic types of their deposits **1**, 688 pp. Jerusalem: Israel Program for Scientific Translations.

Vlasov, K.A., Kuzmenko, M.V. & Es'kova, E.M. 1959: The Lovozero alkali massif, 623 pp. Moscow: Akademiya Nauk SSSR (in Russian). (Translation: Fry, D.G. & Syers, K. 1966 edited by Tomkeieff, S.I. & Battey, M.H.: 627 pp. Edinburgh & London: Oliver & Boyd.)

Wittmann, A. 1970: Germanium. A. Crystal chemistry. In: Wedepohl, K.H. (ed.): Handbook of geochemistry **II/3**, 4 pp. Berlin: Springer Verlag.