

Genthelvite and willemite, zinc minerals associated with alkaline magmatism from the Motzfeldt centre, South Greenland

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Abstract

Two new occurrences of Zn-rich minerals are described from the SM6 lujavrite unit of the Motzfeldt alkaline centre, South Greenland. Zinc and beryllium complexes in the magma gave rise to the formation of interstitial grains of genthelvite ($\text{Zn}_4\text{Be}_3\text{Si}_3\text{O}_{12}\text{S}$), identified in samples by strong green cathodoluminescence. It is suggested that subsequent metasomatism leached Be from the genthelvite, giving rise to the formation of associated willemite (Zn_2SiO_4).

KEYWORDS: willemite, genthelvite, metasomatism, Igaliko, Greenland.

Introduction

THE Motzfeldt centre comprises a series of nested nepheline syenite intrusions and is part of the Igaliko complex of the Gardar province of South Greenland (Emeleus and Upton, 1976; Upton and Emeleus, 1987). The petrology and field relationships of the centre are described by Emeleus and Harry (1970), and in further detail by Jones (1980, 1984), where the SM6 unit is first described. The SM6 unit is a lujavrite (a eudialyte nepheline microsyenite), formed by the accumulation of lujavritic magma underneath large xenoliths of country-rock basalt (Jones, 1980).

Zn-rich minerals are commonly reported from strongly alkaline or agpaite provinces, such as the Khibina massif, USSR (e.g. Shlukova *et al.*, 1980). In the Gardar province, zinc is known in the form of sphalerite (ZnS) (Sørensen, 1962), along with lesser amount of other minerals, such as hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$), genthelvite ($\text{Zn}_4\text{Be}_3\text{Si}_3\text{O}_{12}\text{S}$) (Bollingberg and Petersen, 1967), and willemite (Zn_2SiO_4) (Metcalfe-Johansen, 1977). In addition, zincian nordite is described from a peralkaline trachyte dyke by Upton *et al.* (1976).

Description

Three samples of lujavrite (AM137, AM138 and AM159) were studied and localities of these samples are given in Jones and Larsen (1985). Zn-rich minerals were identified in the lujavrites

using cathodoluminescence (CL), since Zn-rich phases luminesce with characteristic, strong green colour. The identity of the phases was subsequently revealed by electron-probe analysis. Genthelvite was discovered in all of the samples, and is associated with willemite in one rock.

Genthelvite has been found as small interstitial areas up to 0.2 mm across, and disseminated grains of a few microns size throughout all of the samples. In the case of sample AM137, genthelvite is intimately associated with willemite and patches of sericitic and zeolitic alteration. Willemite grains are up to approximately 50 microns across and from the textures are interpreted as secondary. Larger grains of genthelvite can show zoning under CL, and it has been possible to relate these variations to Mn-contents. Less bright zones correlate with higher Mn contents, and hence Mn is acting as a CL-quencher. However, according to Robbins *et al.* (1984), luminescence in willemite arises from Mn-pairing effects, and it may be that there is a maximum CL-brightness at low Mn-concentrations.

Representative analyses of the genthelvites are given in Tables 1 and 2. Due to impossibility of analysis of Be using the electron probe and difficulties with beryllium toxicity in wet chemical analysis, much published data on the compositions of these minerals omit or estimate Be contents. Beryllium is an essential component of genthelvite, and is usually estimated by assuming stoichiometric ratios with other anions (Dunn,

Table 1: New Analyses of Motzfeldt Genthelvitites

	1	2	3	4	5	6	7	8
SiO ₂	34.16	38.51	40.70	36.81	36.32	37.29	41.92	32.34
Al ₂ O ₃	0.84	5.26	6.81	1.89	2.66	5.20	9.68	0.03
FeO	0.08	0.04	0.02	0.07	0.05	0.06	0.05	0.10
ZnO	46.12	41.90	38.69	44.94	43.02	42.32	35.02	54.10
BeO*	11.99	9.33	8.51	9.90	9.50	9.52	7.79	12.39
CaO	0.03	0.03	0.03	0.02	0.01	0.02	0.02	0.00
MnO	5.61	2.33	2.06	4.88	5.28	3.42	4.02	0.73
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
K ₂ O	0.00	0.02	0.04	0.02	0.02	0.03	0.01	0.01
S	5.45	4.48	4.24	5.30	5.05	4.53	4.10	5.49
O=S	2.73	2.24	2.12	2.65	2.52	2.27	2.05	2.75
Total*	101.55	99.66	98.98	101.18	99.39	100.12	100.57	102.44
Analyses to 13 (oxygen and sulphur)								
Si	3.257	3.805	3.992	3.647	3.686	3.720	4.150	3.126
Be	2.743	2.159	2.008	2.353	2.314	2.280	1.850	2.874
Total	6.000	6.000	6.000	6.000	6.000	6.000	6.000	6.000
Al	0.095	0.606	0.786	0.221	0.317	0.609	1.127	0.004
Fe	0.006	0.004	0.002	0.006	0.005	0.005	0.004	0.008
Zn	3.257	3.044	2.811	3.298	3.234	3.127	2.568	3.873
Ca	0.003	0.004	0.002	0.002	0.001	0.002	0.002	0.001
Mn	0.453	0.194	0.171	0.409	0.452	0.288	0.337	0.052
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000
K	0.000	0.004	0.004	0.002	0.002	0.004	0.002	0.002
Total	3.814	3.855	3.777	3.717	4.005	4.035	4.041	3.940
S	0.974	0.824	0.780	0.984	0.961	0.849	0.761	0.994
Cl	0.000	0.001	0.003	0.001	0.002	0.000	0.003	0.000
Total	0.974	0.825	0.783	0.985	0.963	0.849	0.764	0.994

1-4 Motzfeldt genthelvitites, AM137.

5-8 Motzfeldt genthelvitites, AM159.

* - Be contents back-calculated using guidelines in the Appendix

1976). However, as is discussed further below, it appears the stoichiometric relationship of Dunn is violated by the Motzfeldt examples.

Significant Be-substitution for Zn in willemites is possible, due to the isostructural relationship between willemite (Zn₂SiO₄) and phenakite (Be₂SiO₄) (Klaska *et al.*, 1978). Experimental work (Fonda, 1947) has shown that solid solution exists in the willemite structure up to phenakite₄₀. Only Marchenko *et al.* (1976) and Gurvich (1963) give analyses for Be content and show that in those willemites analysed, Be contents can be as much as 0.53%BeO (Gurvich, 1963). The significance of small amounts of beryllium in the crystal structure is great due to the low relative atomic mass of the beryllium atom.

Genthelvite

Genthelvite is an unusual Zn, Be-containing feldspathoid, until now known in the Gardar pro-

Table 2: Published Analyses of Genthelvitites

	1	2	3	4	5
SiO ₂	29.58	30.05	29.78	29.66	31.70
Al ₂ O ₃	n.d.	n.d.	n.d.	n.d.	n.d.
FeO	19.62	10.90	6.14	0.00	7.30
ZnO	26.23	41.73	47.06	54.43	42.40
BeO	13.03*	12.78*	12.69*	12.58*	14.20*
CaO	0.05	0.08	0.05	0.08	n.d.
MnO	7.67	1.85	1.53	0.95	2.90
MgO	n.d.	n.d.	n.d.	n.d.	n.d.
K ₂ O	n.d.	n.d.	n.d.	n.d.	n.d.
S	5.71	5.69	5.65	5.61	5.20
O=S	2.86	2.85	2.83	2.81	2.60
Total	99.03	100.23	100.07	100.50	101.10

1- El Paso County, USA (Dunn, 1976)

2- Jos, Nigeria (Dunn, 1976)

3- W. Cheyenne Canyon, Colorado, USA (Dunn, 1976)

4- Mt. St. Hilaire, Quebec, Canada (Dunn, 1976)

5- Zoned genthelvite, Cairngorm, Scotland (Clark and Fejer, 1976)

* - Calculated assuming (Ca+Fe+Zn+Mn+Mg):Be is 4:3

+ - Constant value after Morgan (1967)

vince only from the apgaitic Ilmausaq intrusion (Bollingberg and Petersen, 1967). The Motzfeldt genthelvite analyses show these to be close to the Zn end-member, with relatively small amounts of MnO (5.6% max.) (Table 1). Unlike all other reported genthelvitites, the Motzfeldt examples show significant aluminium contents (up to 9.7 wt.% Al₂O₃). A plot of wt.% Zn (corrected for Mn and Fe contents; see caption to Fig. 1) against Al in the Motzfeldt genthelvitites (Fig. 1) shows an antipathetic relationship, indicating that Al substitutes for tetrahedral Zn, and not for Be. Si contents are also high, and when recalculated are consistently greater than the stoichiometric 3 Si for 13 oxygens (method of calculation described in the Appendix). These data indicate that Si but only negligible amounts of Al substitute for Be. Genthelvite is isostructural with sodalite (Hassan and Grundy, 1985), and hence the suitability of Si and Al for the Be site is high. The charge misbalance caused by this exchange appears to be accommodated by vacancies in the inter-framework Zn-site. A charge-balance mechanism involving sodium is possible, since interferences between the Na-K α and the Zn-L α radiations mean that this element cannot be separated from the large Zn peaks with the electron probe. However, recalculation of the site-allocations, assuming charge-balancing by vacancies, gives good analytical totals, and does not indicate the presence of an unanalysed element. Because of the Si exchange for Be, and the vacancies in the interframework Zn-site, the calculation

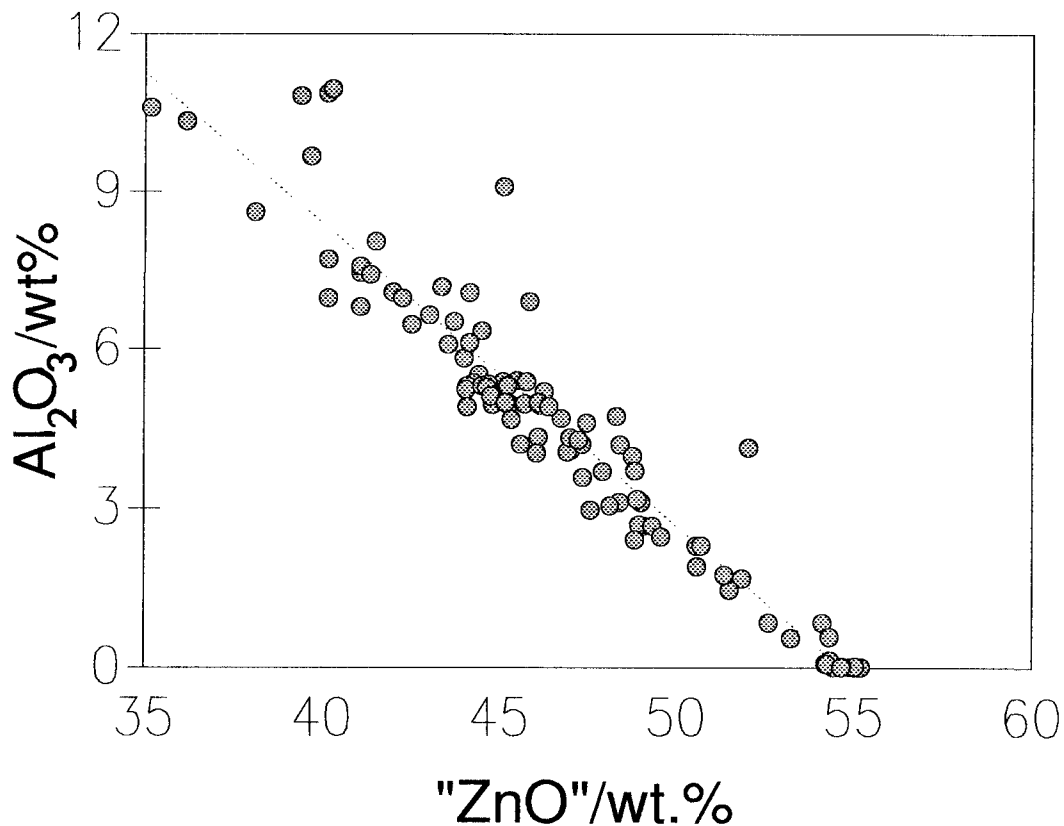


FIG. 1. Graph of wt.% Al₂O₃ against wt.% ZnO in the Motzfeldt genthelvites. The ZnO value is corrected to negate the effects of different helvite group mineral compositions [$'\text{ZnO}' = \text{ZnO} + (81/71) \times \text{MnO} + (81/72) \times \text{FeO}$].

method for helvite group minerals proposed by Dunn (1976), based on stoichiometric relationships between unanalysed Be and total cations, is inapplicable to these examples. A new method for calculation for genthelvites is proposed in the Appendix.

The observations of Dunn (1976) showed that natural helvite-group compositions show a gap between the genthelvite (Zn) and helvite (Mn) end-members. The crystal structures of the helvite group minerals have been determined by Hassan and Grundy (1985), who have shown that cations passively occupy spaces in a sodalite-type framework. Cell dimensions vary little between the end-members of the series, and the compositional gap, therefore, reflects the chemistry of mineralizing fluids, and not a crystal structural control. Fursenko (1982) has gone some way to explaining this phenomenon by relating helvite-group compositions to pH of the mineralizing fluids. He

showed that genthelvites are favoured under alkaline conditions, whereas danalites are formed when fluids are acidic. The Zn,Mn-bearing genthelvites of Motzfeldt therefore indicate high pHs at the time of crystallization. This is confirmed by the presence of eudialyte, which, as has been shown by the experimental work of Christophe-Michel-Levy (1961), decomposes readily in acidic conditions. The presence of helvites, with S²⁻ anions, also shows that redox potentials were below the sulphide/sulphate buffer.

Willemite

Willemite has been described twice before from the Gardar province; first by Bøggild (1953) in a quartz vein from Mussartút, and subsequently from the Ilímausaq complex by Metcalf-Johansen (1977). Willemite from Ilímausaq was considered to have formed by secondary alteration after

Table 3 : Analyses of Willemites

	1	2	3	4	5	6	7	8	9
SiO ₂	27.30	28.30	27.52	27.86	27.70	35.74	25.70	28.70	27.66
Al ₂ O ₃	0.40	0.11	n.d.	n.d.	0.04	6.41	3.33	0.35	5.42
FeO	1.57	2.15 ⁺	n.d.	0.37	0.02	0.36	1.27	1.76	0.16
ZnO	67.58	65.50	73.42	71.51	73.30	56.97	67.51	70.61	65.56
CdO	0.06	0.30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BeO	n.d.	0.25	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CaO	n.d.	n.d.	n.d.	n.d.	n.d.	0.12	0.06	0.04	0.29
MnO	0.85	1.04	0.03	n.d.	0.17	0.07	1.22	0.40	0.87
MgO	1.08	1.16	n.d.	n.d.	0.00	0.14	0.04	0.00	0.21
K ₂ O	0.05	0.08	n.d.	n.d.	n.d.	0.04	0.02	0.04	0.03
Total	99.59^x	99.59[*]	100.97	99.74	101.27^o	99.85	99.15	101.90	100.20
Analyses calculated to 4 oxygens									
Si	1.001	1.020	1.006	1.022	1.008	1.138	0.940	1.025	0.964
Al	0.017	0.005	0.000	0.000	0.002	0.241	0.144	0.015	0.222
Fe	0.048	0.058 ⁺	0.000	0.011	0.001	0.010	0.039	0.053	0.005
Zn	1.856	1.748	1.988	1.944	1.976	1.339	1.823	1.861	1.686
Cd	0.001	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Be	0.000	0.022	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ca	0.000	0.000	0.000	0.000	0.000	0.116	0.002	0.001	0.011
Mn	0.026	0.028	0.001	0.000	0.005	0.071	0.038	0.012	0.026
Mg	0.027	0.063	0.000	0.000	0.000	0.144	0.002	0.000	0.011
K	0.002	0.004	0.000	0.000	0.000	0.042	0.001	0.002	0.001
Total	3.010	2.953	2.995	2.977	2.992	3.095	2.989	2.970	2.926

1,2 - Willemite from the Soviet Union. (Marchenko et al., 1976)

3 - Willemite from the Khibina massif, USSR (Shlukova et al., 1980)

4 - Willemite from Mussartût, Greenland (Bøggild, 1953)

5 - Willemite from Ilfmausaq, Greenland (Metcalf-Johansen, 1977)

6-9 - Analyses of Motzfeldt willemites, AM137.

* - Includes Na₂O=0.03%, H₂O⁺=0.25%, H₂O⁻=0.42%

+ - Calculated as Fe₂O₃

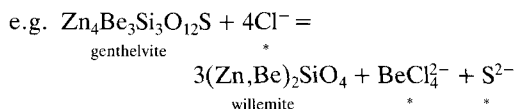
x - Includes Na₂O=0.02%, H₂O⁺=0.68%

o - Includes Cr₂O₃=0.04%

primary sphalerite, by analogy with processes described for its formation at the Franklin Furnace Zn-body. However, the presence of Zn in late-stage volatile-rich fractions can be explained by normal processes of incompatible element enrichment during evolution of alkaline melts, without calling for the primary presence, and subsequent dissolution, of sphalerite. Willemite analyses from Motzfeldt are presented in Table 3 and show significant Al-exchange.

Discussion

The chemical similarities between the genthelvite and willemite at Motzfeldt, and the association of willemite with sericitic alteration, indicate willemite is present as an alteration product of genthelvite. A similar association is described by Marchenko *et al.* (1976) who, from fluid-inclusion work, showed that the willemite owed its presence to metasomatic alteration of genthelvite (with gahnite) at elevated temperatures (450–540°C).

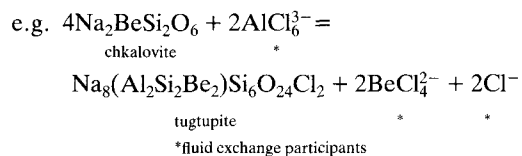


*fluid exchange participants

A metasomatic process of this nature would require the removal of Be from the genthelvite, presumably as complex ions. Studies of Gardar fluid inclusions (Konnerup-Madsen, 1984) have shown methane and carbon dioxide to be present and the latter may be a possible ligand for Be. In addition, the interaction of Cl- and F-rich metasomatic fluids with the Motzfeldt rocks is confirmed by the presence of fluorite-veined sodalite (Finch, in prep.), which is formed by the metasomatic chlorination of nepheline. The sodalite has proved to be secondary, since the transformation of the nepheline results in localized salinity decreases and the precipitation of fluorite. In addition, given alkaline conditions in the system, the tetrahydroxyberyllate (Be(OH)₄²⁻) ion is also a possibility. The matter of beryllium speciation

in alkaline systems has been studied by Novoselova and Simanov (1955), who found that complexes with the formulae BeF_3^- , BeF_4^{2-} , BeCl_4^{2-} and $\text{Be}(\text{CO}_3)_2^{2-}$ are possible, in addition to $\text{Be}(\text{OH})_4^{2-}$.

A similar process of Be-removal can be shown in the chkalovite albitites of the neighbouring Ilímausaq complex, where cores of chkalovite are surrounded by mantles of the beryllium sodalite, tugtupite (Sørensen *et al.*, 1967):



This process is demonstrably a removal of Be by fluids under alkaline conditions. The Ilímausaq intrusion stands out in studies of fluid inclusions across the Gardar (Konnerup-Madsen, 1984), in that carbon dioxide is replaced by methane in the inclusions. Be-transport solely by $\text{Be}(\text{CO}_3)_2^{2-}$ complexes may therefore be ruled out.

Sørensen *et al.* (1967, p. 34) noted that tugtupite and genthelvite co-exist at Ilímausaq, and hence willemite and tugtupite formation by leaching of Be, although analogous processes, occur under different conditions.

Conclusions

Genthelvite crystallized in lujavritic magma, trapped beneath basaltic country rock xenoliths. Formation of helvite-group minerals was made possible by low redox potentials in the system, which allowed formation of S^{2-} ions. Genthelvite formation was favoured over other helvite group minerals since pH levels were significantly alkaline. Subsequent metasomatism led to the leaching of Be from genthelvite, giving rise to the formation of willemite. Transportation of Be in this way is a process comparable to that involved in tugtupite formation from chkalovite in the neighbouring Ilímausaq intrusion.

Acknowledgements

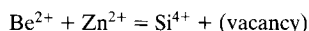
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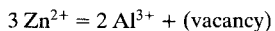
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Appendix: Calculation of genthelvite site allocations

From the formula of genthelvite, $(\text{Zn}, \text{Mn}, \text{Fe}, \text{Al}, \text{vacancy})_4(\text{Be}, \text{Si})_3\text{Si}_3\text{O}_{12}\text{S}$, site allocations in genthelvites may be calculated assuming that Si and Al substituting for either Be or Zn are charge-balanced by vacancies in the Zn-site.





Al is assumed to substitute for Zn, and negligible substitution takes place of Al for Be. This is suggested by the linear relationship expressed in Fig. 1. The expression

$$\frac{4[\text{Si}] - 3([\text{Zn}] + [\text{Mn}] + [\text{Fe}] - 3/2[\text{Al}])}{7}$$

represents the proportion of total Si which substitutes for Be, where e.g. [Si] represents the wt.% of SiO_2 divided by its relative molecular mass. Si minus this expression is therefore equivalent to 3 oxygen in the formula, and hence the factor by which element needs to be multiplied to give the number of atoms in the site allocations is this expression divided by 3. Wt.%Be may then be estimated assuming that $\text{Si} + \text{Be} = 6$.