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Niocalite and wöhlerite from the alkaline and carbonatite rocks at Kaiserstuhl, Germany

THE relatively rare Nb and Zr silicates niocalite (essentially $(\text{Ca},\text{Nb})_4\text{Si}_2\text{O}_7(\text{O},\text{OH},\text{F})_2$), and wöhlerite (essentially $(\text{Na},\text{Ca},\text{Nb},\text{Zr})_4\text{Si}_2\text{O}_7(\text{O},\text{OH},\text{F})_2$) were identified in silicate-carbonate rocks of the central sövite intrusion in the Kaiserstuhl alkaline, carbonatite complex. This is only the second confirmed occurrence of niocalite. It was originally described from sövitic carbonatites in Oka, Quebec, Canada (Nickel, 1956; Nickel *et al.*, 1958), and recently tentatively identified as very small ($<5\ \mu\text{m}$) inclusions in the sodium-calcium carbonate phenocrysts of natrocarbonatite from the 1993 eruption of Oldoinyo Lengai (Church and Jones, in press). Wöhlerite has been mainly described from alkaline rocks, but more recently, Mariano (1989) and Mariano and Roeder (1989) have reported wöhlerite from several carbonatite occurrences, including Oka. In Oka however, niocalite and wöhlerite do not co-exist, unlike at Kaiserstuhl. Wöhlerite is described here from the Kaiserstuhl for the first time.

The Kaiserstuhl alkaline complex is Miocene in age (approximately 18–15 Ma), centred in, and related to the Tertiary Rhinegraben rift valley. The most voluminous alkaline rocks are tephrites and essexites. Of the carbonatites, sövite forms the core of the eroded centre of the complex (Wimmenauer, 1963, 1966; Keller, 1984). It is intrusive into essexites, ledmorites and phonolites. In addition to sövite, there are numerous alvikitic dykes and extrusive carbonatitic lapilli-tuffs (Keller, 1981; Lehnert, 1989).

Niocalite and wöhlerite occur in calcite-silicate rocks of varying mineralogical composition in which calcite, clinopyroxene, hauyne and melanite are associated with wollastonite, åkermanitic melilite, and nepheline or alkali feldspar. These mixed carbonate-silicate rocks form the western margin of the central sövitic carbonatite intrusion in the Kaiserstuhl. They were previously described as calc-silicates (Wimmenauer, 1963), but are considered to represent a magmatic border facies of the sövite intrusion. The exact relationship to the sövite is still unclear due to very limited exposure. Coordinates of the major outcrop areas sampled for this study are the western Badberg (r 34.01.180/ h 53.29.150) and the

upper Badberg (r 34.01.200/ h 53.29.400). The chemical compositions of the host rocks vary considerably because of the heterogeneous nature of these rocks. Of the trace elements, Sr concentrations are high (2600–4400 ppm) and are consistent with their carbonatitic affiliation; however, Nb concentrations are relatively low at 300–500 ppm. In addition to niocalite and wöhlerite, the carbonatites at Kaiserstuhl host several other Nb- (and Zr-) bearing accessory minerals including pyrochlore, Nb-rich perovskite (Wimmenauer, 1966; van Wambeke, 1980; Keller, 1984), Nb-rich zirconolite and calzirtite (Keller, 1984; Lehnert, 1989; Keller *et al.*, 1990).

Niocalite was identified in thin section as accessory grains up to 100 μm in diameter and interstitial to the major mineral phases of the rocks. Mineral separation yielded concentrates from which 21 grains of niocalite and/or wöhlerite were analysed. A total of 71 microprobe spot analyses were obtained on these grains using a Cameca SX50 wavelength-dispersive microprobe situated at the Natural History Museum, London. Operating conditions were 20 kV accelerating voltage and 20 nA current measured on a Faraday cup.

Representative analyses of niocalite and wöhlerite are presented in Table 1, together with examples from the literature, and new analyses of the original material from Oka. Niocalite from Oka is unzoned, and these new data compare reasonably well with those originally reported by Nickel *et al.* (1958), but include also 1.17% $\Sigma\text{REE}_2\text{O}_3$, 0.57% Ta_2O_5 and 0.33% ZrO_2 . Eby (1975) and Hornig (1988) also recognised the presence of REE in niocalite from Oka.

Of the 21 grains examined from the Kaiserstuhl, niocalite was observed in seven grains (representative analyses 1 and 2, Table 1), and wöhlerite in six grains (analyses 5 and 6), and the two minerals intergrown one with the other in eight grains (analyses 3, 4, 7, and 8). Some intergrown grains displayed irregular zoning, observed in backscattered images, which corresponds to compositions intermediate between niocalite and wöhlerite. We are unable to discount the possibility that these intermediate compositions may be due to sub-micron

TABLE 1. Representative analyses of niocalite and wöhlerite

Analysis	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	30.01	29.79	29.35	29.38	29.53	29.54	29.25	30.74	29.57	29.77	29.90	29.92
TiO ₂	0.06	0.10	0.10	0.10	0.57	0.06	0.30	0.40	0.15	0.15	0.26	0.74
ZrO ₂	0.23	0.53	1.21	0.66	12.41	12.97	11.79	12.10	5.60	0.33	—	14.98
HfO ₂	<.15	<.15	<.15	<.15	<.15	<.15	<.15	<.15	<.15	<.15	—	0.17
Nb ₂ O ₅	16.77	16.27	16.85	17.20	16.82	16.81	15.17	14.98	15.99	17.14	18.86	15.01
Ta ₂ O ₅	0.14	0.79	0.23	0.29	0.35	0.14	0.68	0.22	0.16	0.57	—	0.21
Al ₂ O ₃	—	—	—	—	—	—	—	—	—	<.1	0.16	0.00
Y ₂ O ₃	<.05	<.05	0.25	0.31	<.05	<.05	0.14	0.07	<.05	<.05	—	0.06
La ₂ O ₃	0.53	0.38	0.23	0.17	0.07	<.05	0.08	<.05	0.21	0.24	—	0.03
Ce ₂ O ₃	1.30	0.78	0.38	0.56	0.16	0.09	0.05	0.10	0.41	0.67	—	0.05
Nd ₂ O ₃	0.33	0.29	<.15	0.27	<.15	<.15	<.15	<.15	0.18	0.26	—	—
FeO	0.44	0.53	0.27	0.24	0.47	0.49	0.33	0.38	0.37	0.34	0.49	0.28
MnO	0.49	0.48	0.62	0.73	0.47	0.38	0.44	0.54	0.42	0.99	0.99	0.19
MgO	0.18	0.18	0.21	0.14	0.11	0.14	0.13	0.95	0.15	0.23	0.70	0.12
CaO	46.19	46.28	46.76	46.30	29.84	30.51	32.55	29.94	42.25	46.39	46.96	26.39
SrO	0.21	0.20	0.18	0.28	0.13	<.05	<.05	0.12	0.39	0.29	—	0.20
Na ₂ O	0.81	0.71	1.00	0.94	6.96	7.35	6.13	7.31	2.65	0.67	0.55	7.59
F	1.68	2.25	1.90	2.02	1.50	1.60	1.57	1.71	1.55	1.79	1.73	1.92
total	99.37	99.55	99.54	99.59	99.39	100.08	98.61	99.56	100.05	99.83	100.60	97.86
-O=F	0.71	0.95	0.80	0.85	0.63	0.67	0.66	0.72	0.65	0.75	0.73	0.81
H ₂ O	—	—	—	—	—	—	—	—	—	—	0.18	—
Total	98.66	98.60	98.74	98.74	98.76	99.40	97.95	98.84	99.40	99.08	100.05	97.05
ΣY+RE ₂ O ₃	2.16	1.45	0.61	1.00	0.23	0.09	0.13	0.10	0.80	1.17	0.00	0.08
Cations to 36 oxygens												
Na ⁺	0.418	0.368	0.517	0.486	3.638	3.822	3.232	3.774	1.372	0.345	0.279	4.007
Sum Na	0.418	0.368	0.517	0.486	3.638	3.822	3.232	3.774	1.372	0.345	0.279	4.007
Ca ²⁺	13.230	13.221	13.360	13.241	8.621	8.765	9.484	8.543	12.086	13.224	13.158	7.699
Fe ²⁺	0.098	0.118	0.060	0.054	0.106	0.110	0.075	0.085	0.083	0.076	0.107	0.064
Mn ²⁺	0.111	0.108	0.140	0.165	0.107	0.086	0.101	0.122	0.095	0.223	0.219	0.044
Mg ²⁺	0.072	0.072	0.083	0.056	0.044	0.056	0.053	0.377	0.060	0.092	0.273	0.049
Sr ²⁺	0.033	0.031	0.028	0.043	0.020	0.000	0.000	0.019	0.060	0.044	0.000	0.032
Y ³⁺	0.000	0.000	0.035	0.044	0.000	0.000	0.020	0.010	0.000	0.000	0.000	0.009
La ³⁺	0.052	0.037	0.023	0.017	0.007	0.000	0.008	0.000	0.021	0.024	0.000	0.003
Ce ³⁺	0.127	0.076	0.037	0.055	0.016	0.009	0.005	0.010	0.040	0.065	0.000	0.005
Nd ³⁺	0.032	0.028	0.000	0.026	0.000	0.000	0.000	0.000	0.017	0.024	0.000	0.000
Sum Ca	13.754	13.691	13.767	13.700	8.922	9.026	9.746	9.164	12.462	13.773	13.757	7.904
Zr ⁴⁺	0.029	0.068	0.157	0.086	1.632	1.696	1.564	1.571	0.729	0.043	0.000	1.989
Hf ⁴⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.013
Sum Zr	0.029	0.068	0.157	0.086	1.632	1.696	1.564	1.571	0.729	0.043	0.000	2.002
Nb ⁵⁺	2.027	1.961	2.031	2.075	2.050	2.038	1.865	1.803	1.930	2.062	2.230	1.848
Ta ⁵⁺	0.010	0.057	0.017	0.021	0.026	0.010	0.050	0.016	0.012	0.042	0.000	0.016
Ti ⁴⁺	0.012	0.020	0.020	0.020	0.116	0.012	0.061	0.080	0.030	0.030	0.051	0.152
Sum Nb	2.049	2.038	2.068	2.116	2.192	2.060	1.977	1.899	1.972	2.134	2.281	2.015
Si ⁴⁺	8.023	7.942	7.826	7.841	7.962	7.921	7.954	8.184	7.894	7.920	7.819	8.146
Al ³⁺	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.049	0.000
Sum Si	8.023	7.942	7.826	7.841	7.962	7.921	7.954	8.184	7.894	7.920	7.868	8.146
F ⁻	1.420	1.897	1.602	1.705	1.279	1.357	1.350	1.440	1.309	1.502	1.431	1.653

Pr, Sm, Gd, Dy below microprobe detection limit

Analyses 1,2 Niocalite from homogeneous grains

Analyses 3,4 Niocalite from composite niocalite-wöhlerite grains

Analyses 5,6 Wöhlerite from homogeneous grains

Analyses 7,8 Wöhlerite from composite niocalite-wöhlerite grains

Analysis 9. Intermediate composition from a composite grain

} from Kaiserstuhl

Analysis 10. Niocalite from Oka (This study, mean of 12 spot analyses).

Analysis 11. Niocalite from Oka (Nickel *et al.*, 1958)

Analysis 12. Wöhlerite from Prairie Lake (Mariano and Roedder, 1989)

intergrowths of niocalite and wöhlerite, however care was taken to ensure that the analysis spot positions corresponded to areas which appeared homogeneous in the backscattered electron images. Analysis 9, Table 1, is an example of such an intermediate composition.

Niocalite and wöhlerite belong to a family of minerals which includes also cuspidine, hiortdahlite and låvenite. These minerals have many structural

similarities which can only be resolved unambiguously by detailed single crystal X-ray studies. Much of the recent detailed structural work on this group of minerals, particularly by Mellini (1981, 1982) and Merlino and Perchiazzi (1985, 1987, 1988), has shown there to be 8 octahedral (or pseudo-octahedral) cation sites present. A general formula of these minerals on the basis of 36 oxygens is $X_{16}(\text{Si}_2\text{O}_7)_4(\text{O},\text{OH},\text{F})_8$, where X corresponds to

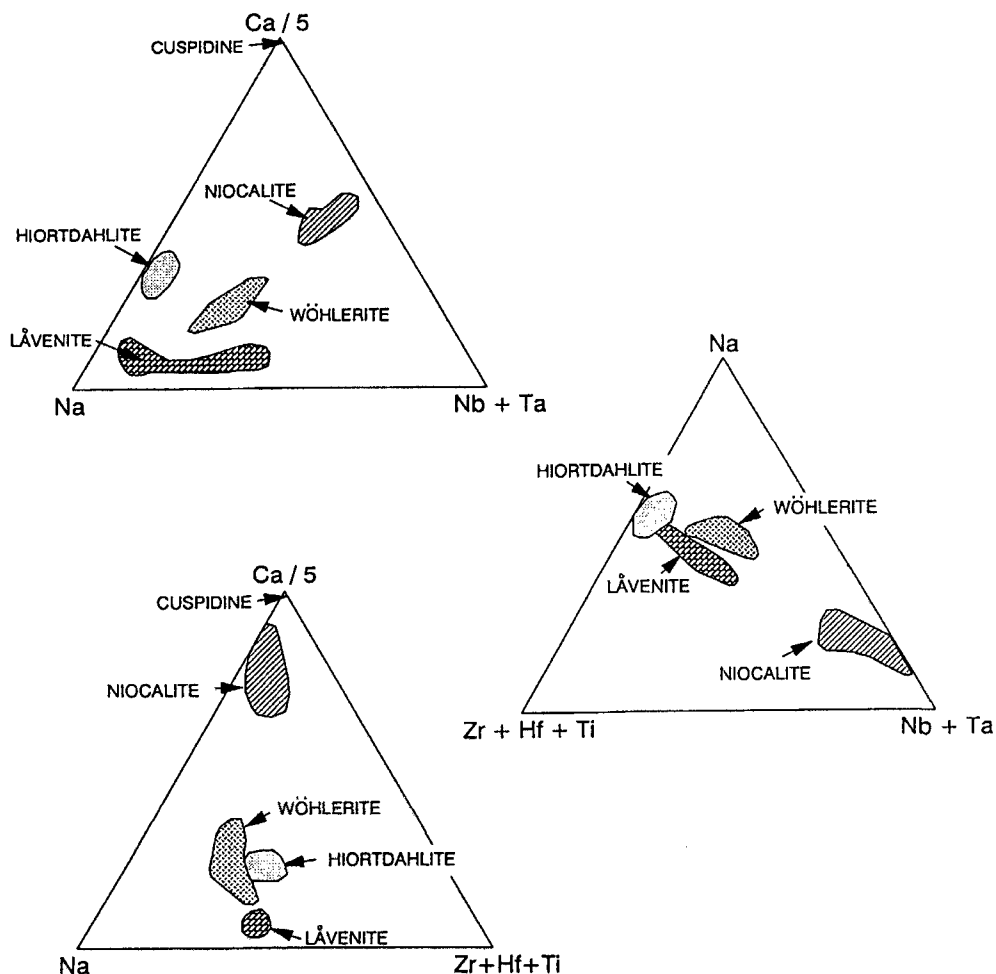


FIG. 1. Ternary diagrams with apices as combinations of Na, Ca/5, Nb+Ta and Zr+Hf+Ti, as cations for minerals of the cuspidine group. Compositional fields for each mineral based on 71 microprobe analyses from this study, and from 28 analyses from the literature. Literature sources are: for cuspidine from Skye, and Vesuvius (Tilley, 1947), from Franklin (Leavens *et al.*, 1987); niocalite from Oka (Nickel *et al.*, 1958; Mellini, 1982); wöhlerite from Angola, Brevik, Guyana, Oka, and Prairie Lake (Mariano and Roeder, 1989), from Junguni (Woolley and Platt, 1988); hiortdahlite from Jingera, Langesund, Tuva, and Vesuvius (Eggleton *et al.*, 1979), from Kipawa (Aarden and Gittins, 1974), from Langesund (Brögger and Cleve, 1889); låvenite from Burpala, Lovozero, S. Norway, and Central Tutarisk massif (in Portnov and Siderenko, 1977), from Tenerife (Ferguson, 1978).

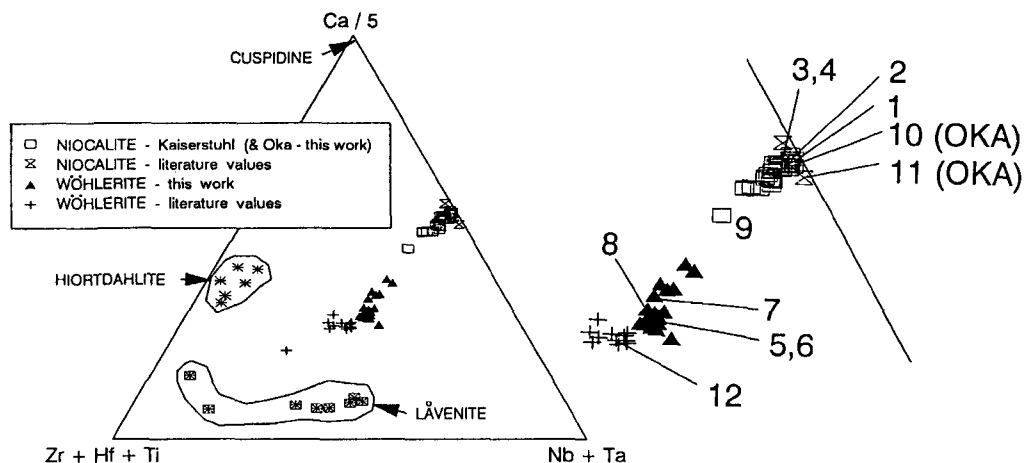
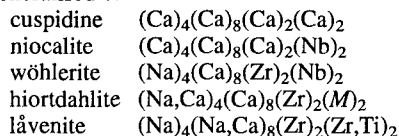


FIG. 2. Ternary diagram of Ca/5, Nb+Ta, Zr+Hf+Ti with individual data points corresponding to the 71 analyses of this study, together with literature values. Numbers refer to analyses quoted in Table 1. Literature sources as for Fig. 1.



which occupy the 16 cation sites. The distributions of these cations within the different minerals can be generalised to:



(where *M* represents a mixing site, in hiortdahlite, with average charge of three, Merlino and Perchiazzi, 1985).

In terms of their complex chemical compositions, minerals in the family can be distinguished by variations in their Ca, Na, Nb (+Ta) and Zr+Ti (+Hf) contents. Of the four possible combinations of cations which can be used as apices on ternary plots, the triangular diagram (Ca/5)–(Zr+Hf+Ti)–(Nb+Ta) has been selected as showing the best chemical discrimination for minerals of this group (Figs. 1 and 2).

The data points on Fig. 2 represent individual analyses of niocalite and wöhlerite from this study, and of these minerals plus cuspidine, hiortdahlite and låvenite taken from the literature. The numbered points in Fig. 2 relate to analysis numbers in Table 1.

Although pure end-member compositions of each mineral apparently do not occur in nature, intermediate compositions are uncommon, and coexisting minerals have not previously been reported.

Conclusions

The second occurrence of the Ca, Nb silicate mineral niocalite, originally described from carbonatites at Oka, Quebec, is reported here from the Kaiserstuhl carbonatite complex, Germany. Niocalite is associated with, and, in some cases, intergrown with the Na, Ca, Zr silicate wöhlerite. Microprobe analyses of both minerals are presented, and their compositions discussed in relation to other minerals of the cuspidine group.

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The effect of fluorine and titanium on the vapour-absent melting of phlogopite and quartz

Introduction

THE reaction biotite + quartz = orthopyroxene + K-feldspar + V or orthopyroxene + L, has been considered as one of the important model reactions applicable to the melting of common crustal rock types (Clemens and Wall, 1981; Grant, 1986). An end-member equivalent of this reaction $ph + qtz = en + L$ was studied by several working groups, but with lack of consensus on the P – T location of the melting curve (Bohlen *et al.*, 1983; Peterson and Newton, 1989a; Montana and Brearley, 1989; Vielzeuf and Clemens, 1992 and Clemens, 1983). Synthesised phlogopite was used as the starting material in all these studies and results have been used to discuss P – T conditions of anatexis and melt compositions, although a synthetic end-member phlogopite is not quite comparable to a natural biotite from high-grade terrain, which contains substantial fluorine substituting for hydroxyl ion and significant amounts of Ti.

This suggests that melting equilibria involving F- and Ti-bearing micas may be closer analogues to melting at lower crustal levels. Peterson *et al.* (1991) made the first study of this reaction using synthetic fluor phlogopite with 60 mole % of F substituting for OH. They found an increase in the incongruent melting temperatures by about 170°C as compared to the average temperatures reported earlier for the same reaction with F-free hydroxy phlogopite. In this communication we report the incongruent melting equilibria in the system phlogopite + quartz, where a natural phlogopite, containing both F and Ti, has been used.

Experimental conditions

Experiments were performed in a 1.25 cm diameter piston cylinder apparatus using talc and pyrex cell. Both piston-in and piston-out techniques were used

and a 13 % pressure correction was made based on the comparative values obtained in the gas bomb. Temperature was measured using Pt/PtRh₁₃ thermocouples and is within 10°C of the reported values. None of the runs were reversed. The starting mixture contained natural phlogopite (supplied by M/S Wards) and natural quartz in equal mass proportion, ground in acetone for 20 minutes. About 40 mg of this mixture was sealed in platinum capsules (2.5mm diameter and 4.5mm long). At P – T points where unseeded experiments yielded phlogopite + melt and phlogopite + enstatite + melt, runs were repeated using starting material seeded with 10 wt.% synthetic enstatite. Phases in starting materials and run products were identified with X-ray powder diffraction, polarising microscope and beginning of melting and extent of reaction were determined using BSE imaging. Sanidine was not identified in any of the runs. Quantitative analysis of starting phlogopite and phases in run products were obtained on CAMECA SX-50 electron microprobe using WDS method (Tables 1 and 3) with 15 kV accelerating voltage and 15 nA beam current. The counting time for each element was 10s. Major element counts were calibrated against a set of synthetic and natural mineral standards (courtesy of Ian Steele, University of Chicago). Fluorine analyses were obtained for phlogopite and melt phases using a TAP crystal. Fluorite (48.66 wt.% F) was used as standard and the concentration of F was determined by collecting counts over 60s time intervals. Beam size was 2 µm in all cases. The starting phlogopite analysis was recalculated using the program GEO/ML to determine H₂O.

Results and discussion

The experimental results are given in Table 2 and the melting curve obtained is plotted in Fig 1. The fluid-