First Terrestrial Occurrence of Roedderite in Volcanic Ejecta of the Eifel, Germany

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Abstract. Idiomorphic crystals of roedderite occur in melt-coated cavities of xenoliths of contact-altered quartz-sillimanite and quartz-feldspar gneisses which were ejected with the tephritic lava of the Bellerberg volcano. Physical and chemical properties of three different sets of crystals agree generally with those of roedderites from meteorites, in which so far the mineral had been found exclusively. In detail, however, there are characteristic chemical differences amongst the Eifel roedderites with one set of crystals matching closely the ideal formula $(Na,K)_2Mg_5 Si_{12}O_{30}$, a second set containing excess alkalies according to the substitution $Na^+ \rightarrow 0.5 Mg^{2+}$, and a third set richer in iron having an alkali deficiency following $Fe^{3+} \rightarrow Fe^{2+} + Na^+$.

The terrestrial roedderites are considered to be precipitates from highly alkaline, MgSi-rich, but Al-deficient gas phases that evolved through contact heating of the gneisses by the tephrite magma.

Roedderite belongs, together with several other rare silicate phases, to the milarite group of minerals. The crystal structure of this group is characterized by six-membered double rings of (Si,Al)-tetrahedra, which are linked through additional, more distorted, tetrahedra to form a three-dimensional tetrahedral framework (Khan et al. 1972). Within the milarite group there are close chemical relationships between roedderite and the minerals merrihueite (Dodd et al. 1965), osumilite (Miyashiro 1956), and yagiite (Bunch and Fuchs 1969), so that all four may be combined to an osumilite subgroup. These relationships were specified by Berg and Wheeler (1976). It is also interesting to note that merrihuite and yagiite are thus far only known from meteorites, whereas osumilite has often been found in volcanic environments and indeed occurs in some of the ejecta from the Eifel as well (Hentschel et al. 1977), although it was not found to coexist with roedderite.

Introduction

Roedderite was first described as a new silicate mineral by Fuchs et al. (1966) from the Indarch meteorite, and soon afterwards Olsen (1967) found it also in the Wichita County meteorite. Seifert and Schreyer (1969), who studied the stability of the related synthetic phase $K_2Mg_5Si_{12}O_{30}$, hypothesized, therefore, that the mineral may be restricted to extraterrestrial materials sufficiently poor in Al, whereas the omnipresence of this element in terrestrial rocks cannot provide the appropriate chemical environment for roedderite formation. Nevertheless, roedderite was recently detected in beautiful crystals in a terrestrial, volcanic environment. A short account of this finding was already given by Hentschel et al. (1977).

Occurrence

Roedderite was found in the huge quarry of the extinct Bellerberg volcano situated about 2 km north of Mayen in the eastern part of the Eifel. The coordinates are R 2587800 H 5580200. The volcano is of quaternary age and has erupted lava and cinder of leucite tephrite chemistry containing numerous xenoliths of very different rock types, in which rare, or even new, minerals had been found already in earlier years (Jasmund and Hentschel 1964; Hentschel 1964; Hentschel and Kuzel 1976; Hentschel 1977). Among the xenoliths those carrying minerals of the osumilite subgroup are relatively rare. Nevertheless, these minerals are highly variable regarding their coloration (Hentschel 1977). In addition to deep blue specimens, which according to Hentschel et al. (1977) have a chemistry similar to that of the "osumilite-(KMg)" of Tieveragh (Chinner and Dixon 1973), there are lighter blue, reddish brown, yellow or nearly colorless varieties. The yellow crystals investigated, and in one case also the reddish brown ones, proved to be roedderites. The nearly colorless crystals, although otherwise of very similar character, do not correspond with any known min-

Fig. 1. Photomicrograph of euhedral roedderite crystal grown in cavity of xenolith A, Bellerberg, Eifel. The fabric of the material of the cavity wall indicates that the finegrained crystals grew from a melt. Inclusions in roedderite consist mainly of hematite. Crossed nicols

eral of the osumilite subgroup but represent a new species that will be described elsewhere.

Petrography

Thus far roedderite was found in three different xenoliths subsequently called A, B, and C. A and B are light colored, banded rocks which consist mainly of quartz and sillimanite and represent highly altered basement gneisses. They are characterized by numerous pores, vesicles, and continuous cavities with very irregular surfaces, which seem to have formed through expansion related to degassing. Xenolith C ist a light brown, porous quartz feldspar rock with larger quartz lenses. The pore space follows largely planes of the earlier metamorphic fabric.

Roedderite occurs sporadically as euhedral crystals along the walls of the cavities, most rarely in xenolith C. Figure 1 shows that the crystals rest upon and enclose a finegrained crystalline matrix which was formed from a melt formerly coating the cavity. It is not clear as to whether the melt crystallized prior or subsequent to the growth of roedderite. The extremely complicated mineralogy of the xenoliths themselves involving hematite, tridymite, sanidine, spinel, ortho- and clinopyroxenes etc. in addition to quartz and sillimanite is disregarded in the present context.

Physical Properties

In xenoliths A and B roedderites form yellow, transparent crystals, whereas in C they are predominantly reddish brown and not transparent. The size of the crystals is slightly below 1–2 mm.

The morphology of the crystals is governed by the hexagonal prism ($10\bar{1}0$) and the base (0001) with intervening smaller faces of the second prism ($11\bar{2}0$) and the pyramid ($10\bar{1}2$) as shown in Fig. 2. Some crystals also exhibit narrow stripes of the flatter pyramid ($10\bar{1}4$). The crystal habit varies strongly from platy through equidimensional to prismatic with extremely differing habits appearing in directly adjacent crystals. However, thick plates and short prisms are most common.

Under the microscope it can be seen that the non-transparent crystals of specimen C are also yellow and transparent inside. The brown color of the peripheries is due to the presence of minute inclusions of a reddish phase, possibly of hematite.
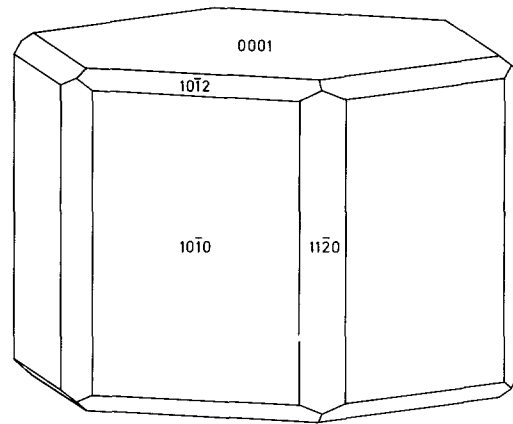
Fig. 2. Morphology of a roedderite crystal from Bellerberg, Eifel

Refractive indices (determined by the immersion method to ±0.001) of the roedderites from samples A and B (Table 1) are nearly identical among themselves, but clearly above those of the roedderites from meteorites. Sample C roedderite has still higher values which must be explained on the basis of varying chemistry.

X-ray powder diffraction patterns of the Bellerberg roedderites are identical with those of the two extraterrestrial roedderites. Table 1 also shows good fit of the lattice constants of these roedderites with those calculated for sample A.

Chemistry

Due to the similarity of many physical constants of members of the milarite group an exact distinction and characterization requires complete chemical analysis. Thus the osumilite subgroup composed of common elements is separated from the remaining minerals which carry essential amounts of rare elements such as Li, Be, Zr, and Ba. Within the osumilite subgroup the cation ratios are critical for further distinction. Thus Bunch and Fuchs (1969) draw a line between the Al-rich minerals osumilite and yagiite

Table 1. Chemical composition, lattice constants, and refractive indices of terrestrial and meteoritic roedderites

	A	B	C	1	2.
SiO_2	71.10	71.32	70.6	71.0	68.0
TiO_2	0.07	0.07	0.07		
Al_2O_3	0.61	0.36	0.50	0.4	2.5
Cr_2O_3	0.00	0.00	0.05		
FeO	0.97	0.49	5.8	2.0	0.4
MnO	0.37	0.31	0.21		
MgO	18.85	17.86	15.7	19.5	19.0
ZnO	0.34	0.00	0.15		
CuO	0.13	0.00	0.03		
Na_2O	3.32	5.29	1.8	4.0	5.3
K_2O	4.33	4.16	4.2	3.3	3.8
Total	100.09	99.86	99.11	100.2	99.0
a_o Å	10.138			10.139	10.127
c_o Å	14.302			14.275	14.245
n_e	1.548	1.558	1.548	1.542	1.543
n_o	1.543	1.545	1.555	1.537	1.536

A. Bellerberg sample A
B. Bellerberg sample B
C. Bellerberg sample C
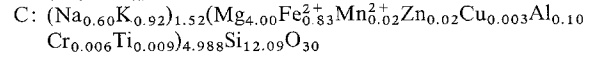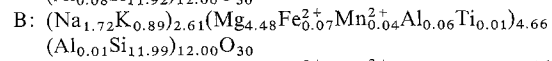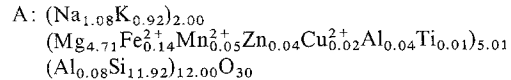1. Indarch meteorite (Fuchs et al. 1966)
2. Wichita County meteorite (Olsen 1967)

with an atomic ratio $Si/Al < 7$ and roedderite as well as merrihueite with $Si/Al > 7$. The latter two phases are defined on the basis of their Na/K- and Mg/Fe-ratios with roedderite having $Na > K$ and $Mg > Fe$. As these criteria should actually yield four rather than two end members, the nomenclature is not complete as yet, but the IMA Commission on New Minerals and Mineral Names is aware of the problem (see Berg and Wheeler 1976).

The chemical compositions of roedderites from the three Bellerberg xenoliths were determined using an electron microprobe (for techniques see Abraham and Schreyer 1973). Table 1 contains one example each out of 18, 2, and 3 analyses of single crystals of samples A, B, and C, respectively. This is permissible because the variations of the roedderites within one xenolith hardly exceed the limits of analytical error. All analyses including those of the meteoritic minerals are rather similar, although there are characteristic differences, especially for the three terrestrial roedderites amongst themselves. Notable are the high iron value for roedderite C which explains its higher indices of refraction, the appearance of copper and zinc in A and C, and, in particular, the varying sodium values of A–C.

The Bellerberg analyses yield the following structural formulae:

A: $(Na_{1.08}K_{0.92})_{2.00}$
$(Mg_{4.71}Fe^{2+}_{0.14}Mn^{2+}_{0.05}Zn_{0.04}Cu^{2+}_{0.02}Al_{0.04}Ti_{0.01})_{5.01}$
$(Al_{0.08}Si_{11.92})_{12.00}O_{30}$
B: $(Na_{1.72}K_{0.89})_{2.61}(Mg_{4.48}Fe^{2+}_{0.07}Mn^{2+}_{0.04}Al_{0.06}Ti_{0.01})_{4.66}$
$(Al_{0.01}Si_{11.99})_{12.00}O_{30}$
C: $(Na_{0.60}K_{0.92})_{1.52}(Mg_{4.00}Fe^{2+}_{0.83}Mn^{2+}_{0.02}Zn_{0.02}Cu_{0.003}Al_{0.10}$
$Cr_{0.006}Ti_{0.009})_{4.988}Si_{12.09}O_{30}$

Thus roedderite of sample A is very close to ideal roedderite, $(Na,K)_2Mg_5Si_{12}O_{30}$. The B sample roedderite has an excess of alkalies, especially of Na which is linked with an R^{2+}-deficiency. The resulting substitution $Na^+ \rightarrow 0.5\ Mg^{2+}$ is a new one for the osumilite-type minerals. Roedderite of sample C, on the contrary, has a deficiency in alkalies, although the contents of divalent cations is close to the ideal 5.0. It is suspected, however, that the iron is not solely present as Fe^{2+} as given but also as Fe^{3+}, because the mineral contains peripheral inclusions of what seems to be hematite. It is likely that the incorporation of Fe^{3+} – or the oxidation of Fe^{2+} to Fe^{3+} – is connected with the alkali deficiency according to the substitution $Fe^{3+} \rightarrow Fe^{2+} + Na^+$ leaving empty alkali sites. Again, a substitution of this type has not been recognized previously for osumilite-type minerals. It is clear that, because of its Na deficiency, the roedderite of sample C does no longer fulfil the requirement $Na > K$ for the name roedderite. Therefore, this phase may actually be looked upon as representing one of the two unnamed members in the subgroup, here with $K > Na$ and $Mg > Fe$.

Discussion

The two synthetic phases most closely related to roedderite are $K_2Mg_5Si_{12}O_{30}$ and $Na_2Mg_5Si_{12}O_{30}$. Both were obtained already some 30 years ago under atmospheric pressure in their respective systems K_2O-MgO-SiO_2 (Roedder 1951) and Na_2O-MgO-SiO_2 (Schairer et al. 1954). Seifert and Schreyer (1969) have determined the pressure temperature stability relations of $K_2Mg_5Si_{12}O_{30}$ under anhydrous as well as hydrothermal conditions. For the latter conditions, which may apply to the stage of vesicle-filling of the xenoliths, the lower thermal stability of $K_2Mg_5Si_{12}O_{30}$ rises from about 550° C at 500 bars water pressure to some 800° C at 6 kbars. At higher water pressures the stability range of $K_2Mg_5Si_{12}O_{30}$ is terminated due to the intersection of the curve of lower stability with the melting curve. For $Na_2Mg_5 Si_{12}O_{30}$ Witte (1975) obtained rather different stability data under hydrothermal conditions: the lower thermal stability increases from about 675° C at 500 bars to some 975° C at 2.5 kbars above which pressure the phase is no longer stable in the presence of a hydrous fluid.

Although not determined, the stability of the ter-

restrial roedderites with intermediate K/Na-ratios as described here probably lies between those of the end members. Thus minimum temperatures as well as maximum pressures are indicated for the formation of roedderites in the xenoliths of the Bellerberg volcano which fit well into the igneous realm. Additional information about temperatures prevailing in the vesicles of the xenoliths during the hottest stage may, in future studies, be obtained through the composition of the melt that coated the vesicle walls. Clearly the temperatures must have been above those of the granitic minimum. It is not certain as to whether the roedderites precipitated from a vapor that coexisted with this melt at peak temperatures or whether they formed from the gas that was released through pressure decrease and/or crystallization of this melt during the uprising of the enclosing lava. Under any circumstance, however, the very occurrence of roedderite in the vesicles indicates that the gas phase present in the xenoliths contained appreciable amounts of alkalies together with Mg and Si, whereas it was probably poor in Fe and especially in Al, which remained in the solids, or in the melt, or were fractionated into solids during crystallization of the melt. The varying chemistry of the three Bellerberg roedderites would thus reflect varying gas compositions which, in turn, are characteristic for each xenolith. Although the argument for Al-poor gas phases as derived purely from the chemistry of the precipitates may be somewhat dangerous, it seems more difficult to assume crystallization of the roedderite as a nearly Al-free mineral from a more aluminous gas, that is to assume Al fractionation into the gas.

It would also seem possible, of course, that the gas phase filling the vesicles is not purely a product of high temperature degassing of the xenoliths themselves, but that it was contaminated by gas of volcanic origin developing from the crystallizing lava. The leucite tephrite lava of the Bellerberg volcano seems well qualified to have evolved such alkaline fluid differentiates. Nevertheless, roedderites have never been detected in vesicles within the tephrite, but are confined to some, and by no means all, basement xenoliths. Strangely enough, two out of three roedderite-bearing xenoliths carry sillimanite and are highly aluminous themselves. Therefore, it is the behavior of the xenoliths within the magma which must hold the key for an understanding of the processes of evolution of the unusual gas phases that precipitated alkali magnesium silicates as terrestrial minerals.

In summary then the first terrestrial occurrences of roedderite are clearly connected with volcanic activity and the related contact heating of basement rocks, in the course of which highly alkaline, MgSi-rich, but Al-deficient gas phases had developed. The roedderites are considered to be the direct and essen-

tially single-phase precipitates from these gas phases during cooling. Thus the "omnipresence" of Al in terrestrial environments that seemed to prohibit roedderite formation is not valid here due to strong Al depletion of the gas.

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