

Zirconolite and baddeleyite from metacarbonates of the Oetztal–Stubai complex (northern Tyrol, Austria)

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ABSTRACT. Zirconolite and baddeleyite from polymetamorphosed metacarbonates of the Oetztal–Stubai complex (northern Tyrol, Austria) are described in terms of their paragenetic relationship and chemical compositions. For the first time an analysis of a chemically zoned niobian zirconolite (high Nb and low Ti in core, low Nb and high Ti at rim) is presented. Genetic possibilities for the origin of the metacarbonates are discussed in the light of zirconolite- and baddeleyite-formation.

KEYWORDS: zirconolite, baddeleyite, Oetztal–Stubai complex, Austria.

THE Oetztal–Stubai complex (northern Tyrol, Austria) is a typical Old Crystalline Basement of the Eastern Alps, mainly consisting of metapelites, gneisses, granites, amphibolites, eclogites, peridotites, and rarely metacarbonates, with a complex metamorphic history. The polymetamorphic situation is fixed by a NNW–SSE overlapping Hercynian and Alpine metamorphism (see Hoinkes *et al.*, 1982, for summary of the metamorphic history of the Oetztal–Stubai complex). The central part of this complex mainly consists of a thick mass of different metabasic units, which have undergone extensive regional Hercynian metamorphism. On the border of this unit, which is essentially surrounded by granitic gneisses, several metacarbonates occur, intercalated within a rock series consisting of amphibolites, metagabbros, eclogites, granites, and peridotites (Hoernes and Hoffer, 1973). These dominantly Hercynian metamorphosed carbonates are extremely mixed with the surrounding rocks, especially the eclogites, which gives evidence for a pre-Hercynian genesis of the eclogites (Miller, 1970; Purtscheller and Sassi, 1975).

This paper is part of a continuing study on the carbonate and eclogitic rocks of the Oetztal–Stubai complex.

Analytical methods. Chemical composition of all mineral phases has been determined using an ARL electron microprobe with four wavelength

dispersive spectrometers at the Department of Mineralogy, University of Innsbruck. An attached energy dispersive system (KeVex) was used only for quick qualitative analyses. All major elements have been corrected for ZAF (Weinke *et al.*, 1974, Chemical Institute, University of Vienna). Rare elements have been corrected only internally and not for major elements, with empirical correction factors according to the method of Bence and Albee (1968), using the factors from Griffin and Amlı (1975). This could cause analytical errors of c.10% in the absolute values of the REE determination. As standards, pure elements (Zr, Hf, Ta) and natural minerals (garnet, kaersutite, jadeite, orthoclase, chromite, spinel, tephroite, gahnite, samarskite) have been used. For the REE synthetic glass standards (Drake and Weill, 1972) were used.

Nomenclature. There exists much confusion in literature regarding zirkelite and zirconolite compositions, formulae and crystal structures (see discussion on nomenclature in Busche *et al.*, 1972, and Mazzi and Munno, 1983). Following Pudovkina and Pyatenko (1969); Pudovkina *et al.* (1975) and Hogarth (1977) zirkelite and zirconolite are synonymous. However, crystal structure and chemical investigations by Mazzi and Munno (1983) showed that zirkelite and zirconolite are identical in chemical formulae and have very similar crystal structures, but 'differ in the stacking of identical pairs of layers of polyhedra'. Since it has been impossible to separate grains of this mineral phase from the Oetztal–Stubai carbonate rocks for X-ray powder investigations (because of its rarity and very small grain sizes), we prefer in this paper the name zirconolite following Borodin *et al.* (1960) who for the first time described a niobian variety of zirconolite, also from carbonate rocks (carbonatites from the Kola Peninsula, USSR).

Results. The metacarbonates consist of the following minerals (in different amounts and

parageneses due to the polymetamorphic nature of the region, mainly representing Hercynian parageneses): carbonate (calcite and/or dolomite), clinopyroxene (diopside), olivine (forsterite), phlogopite, chlorite (clinochlore), ilmenite, spinel, apatite, and various humite minerals. Most metacarbonates contain appreciable numbers of xenoliths (consisting of eclogites, garnet amphibolites, diablastic amphibolites, granitic gneisses, feldspathoids) from 20 cm in diameter to microscopic inclusions.

In several samples (Milchenkar and Pollestal localities), the rare (and for carbonates unusual) minerals zirconolite and/or baddeleyite have been detected during microprobe investigations with the energy dispersive system. Under the petrographic microscope both phases show anhedral grains with almost opaque to dark brown colours. The following mineral assemblages are observed:

1. baddeleyite + zirconolite.
2. zirconolite + chlorite \pm ilmenite \pm apatite.
3. zirconolite + phlogopite + clinopyroxene.
4. zirconolite + ilmenite + calcite \pm phlogopite.
5. zirconolite + ilmenite + phlogopite + clinopyroxene \pm spinel \pm chlorite \pm apatite \pm olivine \pm calcite \pm dolomite.
6. baddeleyite + ilmenite + titanochondrodite.
7. baddeleyite + titanoclinohumite.

All samples contain titanite and/or rutile, but not in direct contact with zirconolite and/or baddeleyite. Zircon has been observed in one sample (PT 38/2) as an inclusion in diopside.

Mineral assemblages 1 and 2 are shown in fig. 1a (BSE picture) and fig. 1b (Nb-L α scanning image): baddeleyite is surrounded by zircono-

lite within a chlorite matrix \pm ilmenite \pm apatite. Mineral assemblage 3 is shown in fig. 2a, where a zirconolite grain is intergrown within phlogopite and clinopyroxene (diopside).

The first three mineral assemblages observed in the Pollestal locality are of special interest because of the textural relationship and chemical composition of zirconolites. The other mineral assemblages are mainly observed in the Milchenkar locality, where zirconolite or baddeleyite coexist with the other minerals (mineral assemblages 4, 5, and 6), except baddeleyite from sample EK 36, which is an inclusion in a titanoclinohumite (mineral assemblage 7, for analyses of titanoclinohumite see Ehlers and Hoinkes, 1984).

Table I presents five analyses of zirconolites from the metacarbonates of central Oetztal-Stubai complex (three from Pollestal and two from Milchenkar) with the structural formula based on seven oxygens, according to the stoichiometric formula $\text{CaZrTi}_2\text{O}_7$, where Ca can be substituted mainly by REE, Mn, U, and Th; Zr by Ti, and Ti by Zr, Nb and Fe. Total cation sums range from 3.962 to 4.060, which is in good agreement with the theoretical formula. Only those elements which lie above the detection limit of the wavelength-dispersive system have been listed; several other elements have also been measured, but were found to lie below the detection limit (Na, K, V, Zn, Sn, W, La, Pr, Tb, Er, Yb, Lu).

Differences in the five zirconolite analyses are seen especially in the values of FeO (ranging from 1.28–5.36 wt. %), REE_2O_3 (ranging from 0.52–5.26 wt. %), TiO_2 (ranging from 25.86–42.64 wt. %) and Nb_2O_5 (ranging from 1.63–16.47 wt. %).

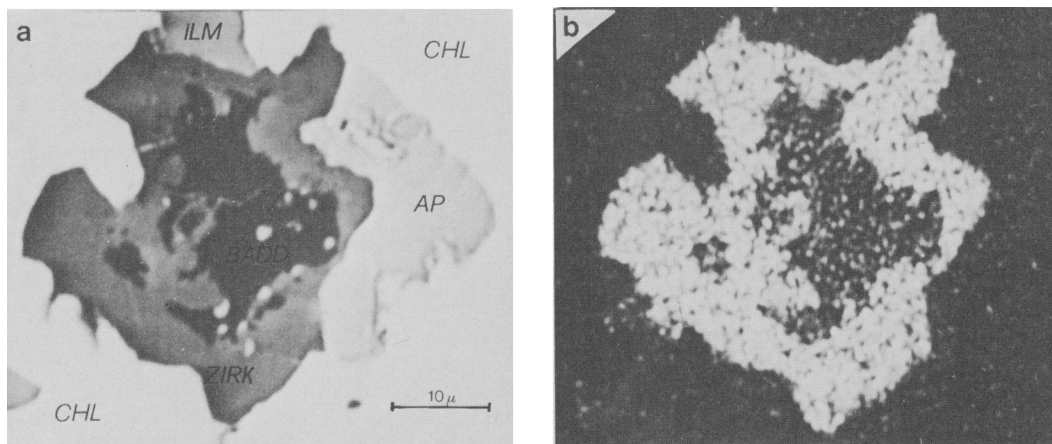


FIG. 1(a) Baddeleyite (BADD) surrounded by zirconolite (ZIRK) in close proximity to chlorite (CHL), apatite (AP), and ilmenite (ILM). Sample PT 9, Pollestal locality, backscattered electron picture. (b) Nb-L α scanning image from baddeleyite-zirconolite assemblage in (a).

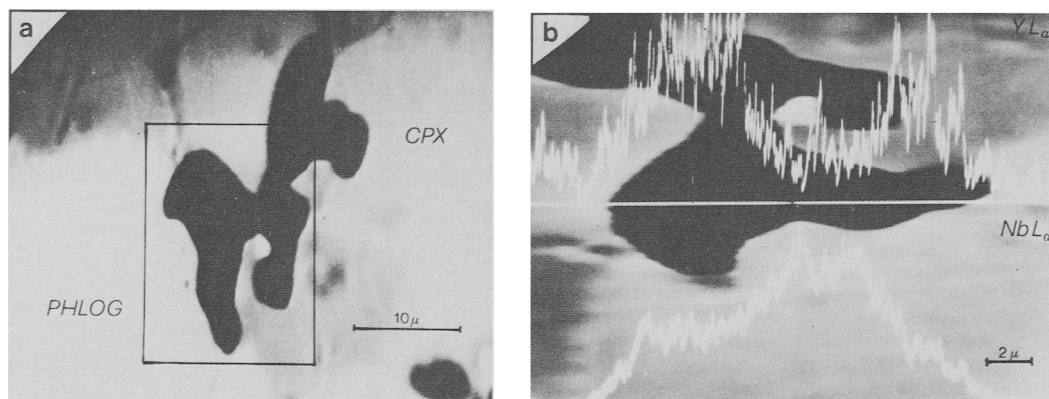


FIG. 2(a) Intergrowth of zirconolite grain with clinopyroxene (CPX) and phlogopite (PHLOG). Sample PT 38/2, locality Pollestal, detail for (b) marked by black square, backscattered electron picture. (b) Backscattered electron picture of zirconolite grain overlain by two scanning profiles (Nb-L α below and Y-L α above the profile line).

Table 1: Electron microprobe analyses of Oetzal zirconolites and structural formulae (based on 7 oxygens) (total Fe as FeO)

	PT9	PT38/2-1	PT38/2-2	EK54	EK8A
CaO	13.39	12.24	10.97	13.94	13.78
MgO	0.30	0.56	0.63	0.22	0.31
FeO	3.12	4.93	5.36	1.28	2.38
MnO	0.81	-	-	-	0.04
NiO	0.02	-	-	-	-
ThO ₂	0.39	1.65	1.38	0.01	0.21
UO ₂	0.02	0.86	0.81	0.07	0.20
Y ₂ O ₃	2.10	-	3.08	0.18	0.14
Ce ₂ O ₃	0.56	0.15	0.46	0.21	0.22
Nd ₂ O ₃	0.04	0.32	0.11	-	-
Sm ₂ O ₃	0.17	-	0.21	0.04	0.03
Eu ₂ O ₃	-	-	0.07	-	0.04
Gd ₂ O ₃	0.41	-	0.32	0.06	0.02
Dy ₂ O ₃	0.34	0.31	1.01	0.09	0.07
Ho ₂ O ₃	-	0.30	-	0.21	-
ZrO ₂	35.35	34.72	35.15	38.64	35.71
HfO ₂	0.69	0.68	0.71	0.77	0.39
PbO ₂	0.11	n.d.	n.d.	n.d.	n.d.
TiO ₂	35.52	25.86	31.12	40.91	42.64
Nb ₂ O ₅	5.94	16.47	5.71	1.63	2.49
Ta ₂ O ₅	0.25	0.95	0.46	-	0.15
SiO ₂	0.06	0.10	0.08	-	-
Al ₂ O ₃	0.98	1.12	1.14	0.80	0.82
Cr ₂ O ₃	0.01	-	-	-	0.02
Total	99.78	101.22	98.78	99.06	99.66
Ca	0.859	0.803	0.735	0.873	0.852
Mg	0.027	0.051	0.059	0.019	0.027
Fe	0.156	0.252	0.280	0.063	0.115
Mn	-	-	-	-	0.002
Ni	0.001	-	-	-	-
Th	0.005	0.023	0.020	-	0.003
U	-	0.012	0.011	0.001	0.003
Y	0.067	-	0.102	0.006	0.004
Ce	0.012	0.003	0.011	0.005	0.005
Nd	0.001	0.007	0.003	-	-
Sm	0.003	-	0.005	0.001	0.001
Eu	-	-	0.002	-	0.001
Gd	0.008	-	0.007	0.001	-
Dy	0.007	-	0.020	0.002	0.001
Ho	-	0.006	-	0.004	-
Zr	1.032	1.037	1.071	1.102	1.005
Hf	0.012	0.012	0.013	0.013	0.006
Pb	0.002	-	-	-	-
Ti	1.599	1.191	1.463	1.799	1.850
Nb	0.161	0.456	0.161	0.043	0.065
Ta	0.004	0.016	0.008	-	0.002
Si	0.004	0.006	0.005	-	-
Al	0.069	0.081	0.084	0.055	0.056
Cr	0.001	-	-	-	0.001
Total	4.030	3.962	4.060	3.987	3.999

One zirconolite grain shows extreme compositional zoning: the core is enriched in Nb (Table I, analysis PT 38/2-1), relative to the rim (Table I, analysis PT 38/2-2; also fig. 2b), whereas Ti is enriched at the rim compared with the core in accord with a Ti-Nb substitution. Core analysis shows a higher CaO (12.24%) and lower REE (1.08%), compared with the rim (CaO = 10.97%, REE = 5.26%), which is due to REE-substitution for Ca.

However, Y does not follow exactly this core-rim relationship: there is enrichment of yttrium near the rims (rim analysis PT 28/2-2, Table II, is from the highest Y-enrichment with 3.08% Y_2O_3) with a further decrease of Y at the rims, which is evident by the Y-X-ray scanning profile in fig. 2b (by monitoring the difference signals of two combined back-scattered electron detectors it has been confirmed that this is not due to uneven polishing). Ti/Zr ratios for the zirconolites are 1.55 for sample PT 9, 1.63 for sample EK 54 and 1.84 for sample EK 8A. In the zoned zirconolite grain Ti/Zr ratio increases from core (1.15) to rim (1.37).

Table II. Electron microprobe analyses of Oetztal baddeleyite (total Fe as FeO)

	PT 9	EK 36
ZrO ₂	96.91	97.88
HfO ₂	1.11	1.01
CaO	0.06	0.03
TiO ₂	0.48	0.07
FeO	0.36	0.06
MgO	0.03	0.08
SiO ₂	0.24	0.10
Cr ₂ O ₃	0.01	-
Al ₂ O ₃	0.03	-
MnO	-	-
NiO	0.01	-
Nb ₂ O ₅	0.05	-
Ta ₂ O ₅	-	n.d.
UO ₂	-	0.13
ThO ₂	-	-
Total	99.29	99.36

Table II shows analyses of two baddeleyite grains. Baddeleyite from sample PT 9 (see fig. 1a and 1b) is an inclusion in a zirconolite grain, baddeleyite from sample EK 36 coexists with ilmenite and titanochondrodite; another baddeleyite from sample EK 36 is an inclusion in a titanoclinohumite and has not been analysed. Comparison of the two analyses shows that baddeleyite from sample PT 9 contains more impurities than baddeleyite from sample EK 36

(0.48% TiO₂ and 0.36% FeO in PT 9, compared with 0.07% TiO₂ and 0.06% FeO in sample EK 36), possibly due to its close proximity to zirconolite. Zr/Hf ratios are 76.3 for sample PT 9 and 84.3 for sample EK 36.

Discussion. Zirconolite (and zirkelite) is a very rare terrestrial mineral and has been reported so far only from a few localities: in a decomposed magnetite pyroxenite in Brazil (Hussak and Prior, 1895); an alluvial placer deposit in Ceylon (Blake and Smith, 1913); amphibolized pyroxenites in the Afrikanda and Arbarastkh Massifs, USSR (Borodin *et al.*, 1957, Wark *et al.*, 1973); carbonatites of Kola Peninsula, USSR (Borodin *et al.*, 1960), Santiago island, Cape Verde Republic (Silva and Figueiredo, 1980) and Kaiserstuhl, Germany (Sinclair and Eggleton, 1982; Keller, 1983, unpublished; Keller, 1984); ultrabasic cumulate of Rhum, Inner Hebrides, Scotland (Williams, 1978); pegmatites of St Kilda, Scotland (Harding *et al.*, 1982); kimberlites in Kimberley, South Africa (Raber and Haggerty, 1979) and sanidinite lava of Campi Flegrei, Italy (Mazzi and Munno, 1983). In lunar basalts zirconolite/zirkelite seems to be a relatively common accessory phase (Lovering and Wark, 1971; Busche *et al.*, 1972; Wark *et al.*, 1973; Meyer and Boctor, 1974).

Baddeleyite is also an uncommon mineral in terrestrial rocks, but not so rare as zirconolite, and has been observed in different placer deposits, gabbro sills, diabase dikes, kimberlites, alkaline, and carbonatitic rocks (Palache *et al.*, 1944; Franco and Loewenstein, 1948; Hiemstra, 1955; Vlasov, 1966; Keil and Fricker, 1974; Siivola, 1977; Scatena-Wachel and Jones, 1984).

A review of all published zirconolite (and zirkelite) analyses shows differences, especially in TiO₂, CaO, ZrO₂, and REE₂O₃. A plot of analyses from literature (and this paper) in a TiO₂-CaO-ZrO₂-triangle (fig. 3) and in a CaO vs. (Y, REE)₂O₃ diagram (fig. 4) provides a possible means for differentiating between zirconolites/zirkelites from various rocks: zirconolites from carbonatites (analyses from Borodin *et al.*, 1960; Silva and Figueiredo, 1980; Sinclair and Eggleton, 1982; Keller, 1983, unpublished analyses, and Keller, 1984), pyroxenites (analyses from Borodin *et al.*, 1957, Vlasov, 1966, and Wark *et al.*, 1973), sanidinite lava (analyses from Mazzi and Munno, 1983) and the Oetztal zirconolites (this paper) differ from those of alluvial placer deposits (analyses from Blake and Smith, 1913), pegmatite (analyses from Harding *et al.*, 1982), kimberlites (analyses from Raber and Haggerty, 1979) and lunar rocks (analyses from Busche *et al.*, 1972; Wark *et al.*, 1973; Roedder and Weiblen, 1973; Meyer and Boctor, 1974; Raber and Haggerty, 1979) by different

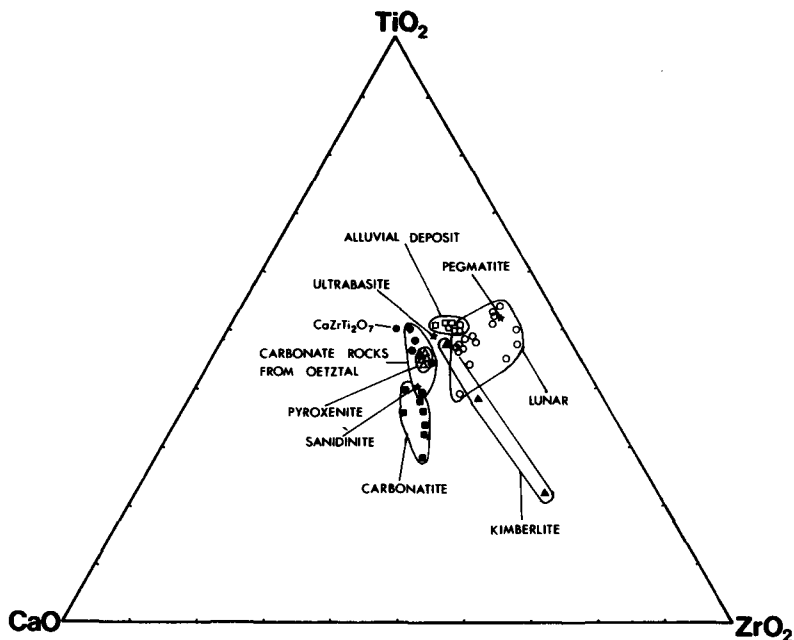


FIG. 3. TiO_2 - CaO - ZrO_2 triangle (mol. %) for various zirconolites and zirkelites.

CaO contents (fig. 3); zirconolites/zirkelites from carbonatites, pyroxenites, sanidinite, and meta-carbonates from Oetztal have more CaO . The zirconolite from the ultrabasic layered cumulate of Rhum (Williams, 1978) is intermediate between the two groups.

Caution should be applied to Mazzi and Munno's (1983) zirconolite from sanidinite lava as the analysis has low totals (76.8%) indicating an unsatisfactory analysis, which could affect its position in fig. 3.

In fig. 4 (CaO vs. $(\text{Y}, \text{REE})_2\text{O}_3$) a remarkable overlap for carbonatite- and Oetztal-zirconolites (and to some extent for zirconolites from pyroxenites) is observed, due to the relatively high CaO and relatively low REE content; zirconolites from other rocks have less CaO and very low (kimberlites) to low (alluvial placer deposit) REE content. Zirconolites from lunar rocks in general have lower CaO and a wide range of REE contents (varying from c.5 to 25%).

Some caution should be applied in the interpretation of fig. 4 concerning the $(\text{Y}, \text{REE})_2\text{O}_3$ values, as only the available data from literature have been plotted and some authors only give values for Y_2O_3 and not for ΣREE , or the analyses do not quote all the REE . However, the positions of the zirconolites from carbonate rocks from Oetztal, carbonatites, kimberlites, alluvial deposits, pyroxenites, and lunar rocks are hardly affected, as

the total sums (min. 98.72%, carbonatitic rock; Silva and Figueiredo, 1980) indicate analyses where almost all important elements have been measured. Only the zirconolites from the ultrabasic layered cumulate of Rhum (Williams, 1978; total sum 93.38%), pegmatite (Harding *et al.*, 1982; total sum 90.82%) and sanidinite (Mazzi and Munno, 1983; total sum 76.8%) are possibly affected (e.g. ΣREE in the Rhum zirconolite is probably in the region of c.5%, indicated by a cation deficiency in the A-position of c.0.22, formula based on seven oxygens, where $A = (\text{Ca}, \text{Mn}, \text{U}, \text{Th}, \text{Y}, \text{REE})$ after Sinclair and Eggleton, 1982), which would shift these positions more to the $(\text{Y}, \text{REE})_2\text{O}_3$ -rich side of the diagram.

As stated above Ti/Zr ratios range from 1.15 to 1.84. The zoned zirconolite grain shows an increase of Ti/Zr ratio from core (1.15) to rim (1.37). According to the zirconolite thermometer (Wark *et al.*, 1973, and Raber and Haggerty, 1979) this implies a decrease of temperature from core to rim in the zoned zirconolite. Actual temperatures have not been calculated because, as stated by Raber and Haggerty (1979), the thermometer gives extensively high temperatures (for kimberlites), which may be the result of this ratio being sensitive also to pressure.

Zirconolite formation and zirconolite zoning may have two reasons: 1. crystallization of zirconolite from a differentiated magma (possibly one

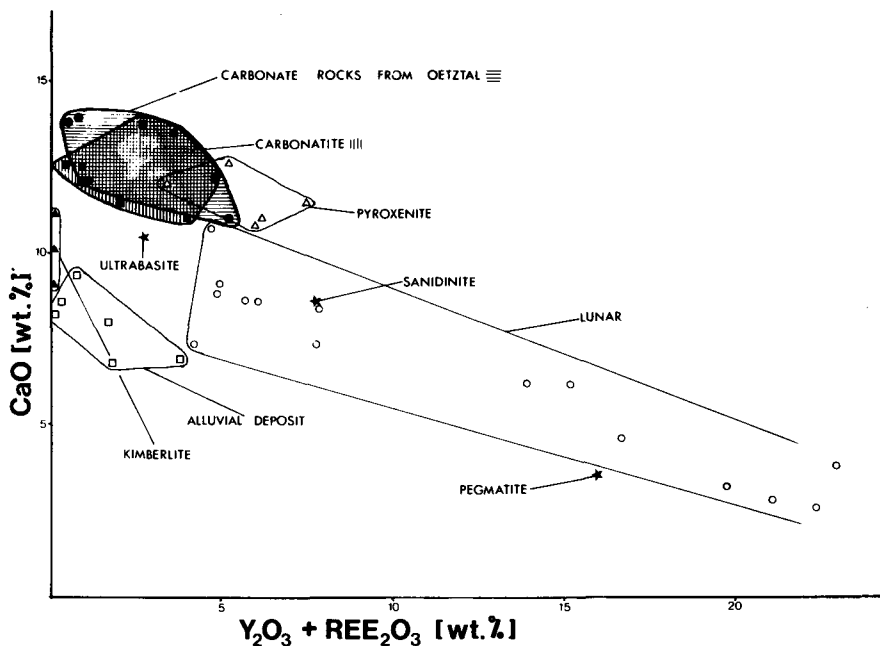


FIG. 4. $\text{CaO}-(\text{Y}, \text{REE})_2\text{O}_3$ diagram (wt. %) for various zirconolites and zirkelites.

of the last crystallizing minerals, mopping up all incompatible elements like Nb, REE, etc., as stated by Williams, 1978), where chemical zoning can be explained by crystallization during localized differentiation or, 2. zirconolite formation by a metamorphic reaction, where chemical zoning can be explained by a possibly continuous reaction.

The chemical evidence indicates that the Oetztal zirconolites are associated with carbonatites (see figs. 3 and 4) which supports the first assumption. On the other hand there is no field evidence for the existence of carbonatites (for example absence of alkali rocks in the surrounding areas), and also current geochemical investigations do not show typical trace element and REE abundances for carbonatites (although these values are also not typical of sedimentary carbonates). According to Raber and Haggerty's (1979) theory, zirconolite formation (in the South African kimberlites) is suggested to be triggered by a carbonatitic fluid, indicated by the presence of calcite at the mineral interfaces. Thus the absence of calcite at the mineral interfaces (although a major component of the rocks) of the zirconolites from the Oetztal samples may indicate that zirconolite formation was not caused by a magmatic process.

There seems to be textural evidence in sample PT 9 for supporting the second assumption, i.e. formation of zirconolite by metamorphic processes,

where baddeleyite is surrounded by zirconolite (fig. 1a). Zirconolite could have been formed by a reaction involving baddeleyite + calcite + a Ti-bearing phase (rutile, ilmenite, titanite), but the complete metamorphic process seems to be more complicated because the existence of baddeleyite implies high temperatures (Butterman and Foster, 1967; Raber and Haggerty, 1979) as it is normally a product of silica-undersaturated rocks of magmatic origin. This is in sharp contrast to the metamorphic history of this region (Hercynian regional metamorphism with maximum temperature of 650 °C and 5 kbar pressure + alpine low-grade overprint).

However, at the present state of investigations on the metacarbonates of the Oetztal-Stubai complex a clear decision on the question of origin of zirconolites and baddeleyites cannot be made and awaits further studies.

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