

Tinzenite, a member of the axinite group with formula revised to $\text{Ca}_2\text{Mn}_4^{2+}\text{Al}_4[\text{B}_2\text{Si}_8\text{O}_{30}](\text{OH})_2$

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Abstract: The official International Mineralogical Association (IMA) list of minerals had given the formula for the tinzenite, an axinite-group mineral, as $\text{Ca}_6\text{Al}_4[\text{B}_2\text{Si}_8\text{O}_{30}](\text{OH})_2$. However, this formula does not correspond to compositions reported for tinzenite, which contain less Ca than the other three members of the axinite group, and significantly more Mn^{2+} than the Mn end-member, axinite-(Mn), $\text{Ca}_4\text{Mn}_2\text{Al}_4[\text{B}_2\text{Si}_8\text{O}_{30}](\text{OH})_2$. Revision of the tinzenite formula to $\text{Ca}_2\text{Mn}_4^{2+}\text{Al}_4[\text{B}_2\text{Si}_8\text{O}_{30}](\text{OH})_2$ was accepted by the IMA Commission on New Minerals, Nomenclature and Classification. A review of the compositions of 68 axinites containing over 10 wt% MnO reveals continuous solid solution between end-member tinzenite and end-member axinite-(Mn). Distinguishing tinzenite from axinite-(Mn) requires an analysis, either wet chemical or electron microprobe accompanied with an estimate of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and assuming stoichiometric H and B. The distinction should be based exclusively on Ca content with the cutoff being $\text{Ca} = 3$ atoms per formula unit (apfu). Compositions closely approaching end-member tinzenite have been found at Klučov near Třebíč, Czech Republic and Jurvielle, Hautes-Pyrénées, France. The presence of tinzenite has been confirmed at ten localities worldwide, at nine of which tinzenite is found with quartz, rhodonite, Mn-bearing calcite or rhodochrosite in veinlets cutting stratiform manganese deposits or metachert. The tenth locality (Klučov) is entirely different: a pegmatite of the niobium-yttrium-fluorine family, where tinzenite occurs with quartz, K-feldspar and cassiterite.

Key-words: axinite group; chemical composition; mineral nomenclature; manganese deposits.

1. Introduction

Tinzenite is one of the four minerals comprising the axinite group. The other three are formulated as $\text{Ca}_4M_2^{2+}\text{Al}_4[\text{B}_2\text{Si}_8\text{O}_{30}](\text{OH})_2$, where $M = \text{Fe}, \text{Mn}, \text{Mg}$, respectively axinite-(Fe), axinite-(Mn) and axinite-(Mg). The official International Mineralogical Association (IMA) list of minerals had given the formula for tinzenite with $M = \text{Ca}$, *i.e.*, $\text{Ca}_6\text{Al}_4[\text{B}_2\text{Si}_8\text{O}_{30}](\text{OH})_2$. However, this formula does not correspond to compositions reported for tinzenite, which contain less Ca than the other three members of the axinite group and significantly more Mn^{2+} than axinite-(Mn). Proposal 16-D for revision of the tinzenite formula to $\text{Ca}_2\text{Mn}_4^{2+}\text{Al}_4[\text{B}_2\text{Si}_8\text{O}_{30}](\text{OH})_2$ was accepted by the IMA Commission on New Minerals, Nomenclature and Classification by analogy with formulae of other axinite-group minerals.

The present paper reviews compositional data on Mn-rich axinite in order to validate this formula for tinzenite, and to illustrate the relationship of tinzenite to axinite-(Mn) and other members of the axinite group.

2. Historical summary

Roth (2007, p. 147) aptly characterized tinzenite, as having “had a turbulent history”. It was first described by Jakob (1923) from Alp Parsettens and Falotta near Tinizong village, Oberhalbstein, Grisons, Switzerland. The mineral was named after the old designation for Tinizong – Tinzen, a village near to the type locality (Roth, 2007). Jakob (1923) gave the formula $4\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Mn}_2\text{O}_3 \cdot 2\text{CaO}$, combining Na_2O , K_2O and H_2O (1.22–1.25 wt% H_2O^+) with CaO. Boron was not sought, and Mn was reported as trivalent. The validity and formulation of tinzenite was challenged by Foshag (1925), provoking a clarification and more analyses (Jakob, 1926). Jakob (1923, 1926, 1933) also attempted to find a compositional basis for the different colors of tinzenite at the type localities. Sanero (1936) reported compositions consistent with $4\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Mn}_2\text{O}_3 \cdot 2\text{CaO}$ for tinzenite from Cassagna, Liguria.

Winchell & Winchell (1951, p. 505) gave the formula for tinzenite as $\text{H}_2\text{Ca}_3\text{Al}_4\text{Mn}_4^{3+}\text{Si}_8\text{O}_{32}$, and inferred a close relationship to thulite on the basis of its composition and properties.

Milton *et al.* (1953) examined a specimen of “type Swiss material” and discovered the presence of boron, while X-ray powder patterns revealed the close relationship with axinite, which was considered one mineral at the time. This relationship led Milton *et al.* (1953) to assume Mn as divalent, and consequently, they proposed the formula $H(\text{Ca}, \text{Mn}, \text{Fe}, \text{Mg})_3\text{Al}_2\text{BSi}_4\text{O}_{16}$ for axinite, citing the lower CaO content in tizenite as a reason for the more generalized formula in preference to $\text{H}\text{Ca}_2(\text{Fe}, \text{Mn})\text{Al}_2\text{BSi}_4\text{O}_{16}$.

Sanero & Gottardi (1968) gave the general formula for axinite as $H(\text{Ca}, \text{Mn}, \text{Fe}, \text{Mg})_3\text{Al}_2\text{BSi}_4\text{O}_{16}$, and proposed on page 1409 that “the name ‘tizenite’ must be used for those axinites with $\text{Ca} < 1.5$ and $\text{Mn} > \text{Fe}$ (but usually $\text{Mn} \gg \text{Fe}$).” On page 1410, they wrote that “finally we do not propose any name of axinites of composition like $\text{H}\text{Ca}_3\text{Al}_3\text{BSi}_4\text{O}_{16}$ [sic] or $\text{H}\text{Fe}_3\text{Al}_2\text{BSi}_4\text{O}_{16}$, which have not been found in nature and, in our opinion, will neither be found nor synthesized (sic).” Assuming an error in the coefficient for Al, the first formula can be doubled and rearranged to give $\text{Ca}_6\text{Al}_4[\text{B}_2\text{Si}_8\text{O}_{30}](\text{OH})_2$.

Basso *et al.* (1973) refined the crystal structure of a tizenite from the manganese deposit at Cassagna, Liguria, Italy, and reported that Ca and Mn were ordered at the two Ca sites with one site entirely occupied by Ca, and the second site occupied 70% by Mn, 30% by Ca.

Belokoneva *et al.* (2001) refined the structure of a tizenite from Falotta and also reported a high degree of order at the two Ca sites: $0.925\text{Ca} + 0.075\text{Mn}$ and $0.495\text{Ca} + 0.505\text{Mn}$. However, they ruled out the possibility of full occupancy of the second Ca site by Mn because of distortions occurring in the borosilicate group, and thus proposed $\text{Mn}(\text{Ca}, \text{Mn})_2\text{Al}_2[\text{BSi}_4\text{O}_{15}](\text{OH})$ as a formula for tizenite.

Back (2014) gave a formula $\text{CaMn}_2^{2+}\text{Al}_2\text{BO}(\text{OH})(\text{Si}_2\text{O}_7)_2$ for tizenite and cited two analyses by Jakob reported in *New Mineral Names* (*American Mineralogist*, 13, p. 202, 1928) as well as Sanero & Gottardi (1968) and Basso *et al.* (1973).

3. Chemical data

The major constituents of axinite-group minerals are SiO_2 , B_2O_3 , Al_2O_3 , Fe_2O_3 , MgO , CaO , MnO , FeO and H_2O , whereas BeO , Na_2O , TiO_2 , V_2O_3 (reported as V_2O_5 by Ragu, 1990), Cr_2O_3 , and ZnO are reported as much subordinate constituents in a few cases (*e.g.*, Grew 1996; Andreozzi *et al.*, 2000, and references cited therein). In general, there is little evidence either for significant deviation in stoichiometry in terms of Si, B and H contents or for substitutions involving these constituents (Basso *et al.*, 1973; Takéuchi *et al.*, 1974; Belokoneva *et al.*, 1997, 2001). Moreover, except for axinite containing the most Mn and least Fe^{2+} and Mg, Ca averages close 4 atoms per formula unit (apfu). Thus, the focus of the present paper will be on the axinites richest in Mn, that is, $\text{MnO} > 10\text{ wt}\%$, close to the 12.46 wt% calculated for end-member axinite-(Mn), which are the only axinites to have $\text{Ca} < 4$ apfu.

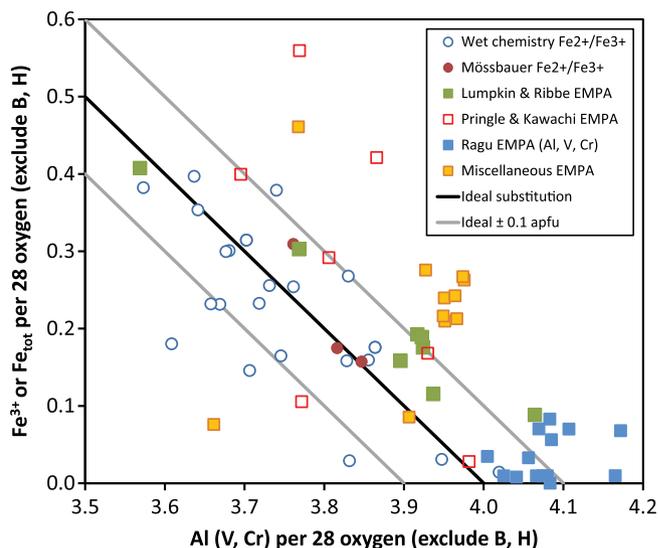


Fig. 1. Plot of 67 analyses of axinite-(Mn) and tizenite containing $> 10\text{ wt}\%$ MnO normalized to 28 oxygen assuming stoichiometric B and H contents. Vanadium and Cr were reported by Ragu (1990) and by Filip *et al.* (2008). Fe^{3+} is differentiated for wet chemical analyses or analyses accompanied by Mössbauer spectroscopic data; total Fe is given for electron microprobe analyses (EMPA). Analyses giving $\text{Si} > 8,12$ or $\text{Si} < 7.88$ per 28 O (excluding B, H) are not plotted, including all the analyses reported by Kayupova (1961) and Dunn (1979). Sources of plotted analytical data: Andreozzi *et al.* (2000); Belokoneva *et al.* (2001); Barsanov (1951); Bottrill (1983); Brusnitsyn *et al.* (1997); Cortesogno *et al.* (1979); Filip *et al.* (2008); Ford (1903); French & Fahey (1972); Fromme (1909); Genth (1891); Getling (1965); Goldschmidt (1911); Kurshakova (1984); Lumpkin & Ribbe (1979); Milton *et al.* (1953); Otroshchenko (1971); Ozaki (1969, 1972); Penco (1964); Penco & Sanero (1964); Pringle & Kawachi (1980); Ragu (1990); (Škoda *et al.*, 2006 and unpublished data).

A major difficulty in treating Mn-rich axinite is distinguishing Fe^{2+} and Fe^{3+} . Few studies report $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio determined by Mössbauer spectroscopy, and wet chemical analyses are not always reliable. Instead of stoichiometric calculations, I have used a plot (Fig. 1) of Fe versus Al (including V and Cr if reported) to determine whether significant Fe^{2+} could be present, in which case it was calculated simply from $\text{Fe}^{2+} = \text{Fe}_{\text{tot}} - (4 - \text{Al} - \text{V} - \text{Cr})$, assuming all Al is in octahedral coordination. Figure 1 shows that the Fe^{3+} contents based on Mössbauer spectroscopy (3 of 3 cases) or on wet chemical analysis (all but 6 cases) plot within the ± 0.1 apfu envelope of ideal stoichiometry, $\text{Fe}^{3+} + \text{Al} = 4$ apfu, justifying using the Fe^{2+} contents reported in these analyses for plotting in Fig. 2. In addition, many electron microprobe analyses (EMPA) also plot within the ± 0.1 apfu envelope of ideal stoichiometry. EMPA plotting above ideal stoichiometry and outside the ± 0.1 envelope could result from the presence of significant Fe^{2+} . In either case, Fe^{2+} can be calculated from $\text{Fe}^{2+} = \text{Fe}_{\text{tot}} - (4 - \text{Al} - \text{V} - \text{Cr})$. When $\text{Al}(\text{Cr}, \text{V}) > 4$ apfu, Fe^{3+} contents are assumed to be negligible.

Sixty-eight analyses with $\text{MnO} > 10\text{ wt}\%$ and a reasonable stoichiometry have been plotted in Fig. 2; axinite-(Mn) containing 0.6–0.7 wt% BeO (Zagorsky *et al.*, 2016) has not been included. The plot reveals no break in solid

Table 1. Localities for tinzenite.

Locality	Associated minerals	Source of data
<i>Localities confirmed by chemical analysis</i>		
Falotta and Alp Parsettens mines near Tinzong (Tinzen), Oberhalbstein, Grisons, Switzerland (type)	Qz, Rdn, Cal, Brt	Jakob (1923, 1926, 1933); Milton <i>et al.</i> (1953); Sanero & Gottardi (1968); Roth (2007)
Gambatesa, Cassagna and two other mines, Val Graveglia, Liguria, Italy	Qz, Rdn, Hrm, Cal, Rds, Hem, Cct, sursassite, bementite, parsettensite, Mn oxides	Pelloux (1935); Sanero (1936); Cortesogno <i>et al.</i> (1979); Marchesini & Pagano (2001)
Kamys deposit, Atasuysk area, central Kazakhstan (“severginite” I)	Cal, friedelite	Kayupova (1961)
Matsukabu deposit, Ananai mine, Kochi Prefecture, Japan	Qz, Cal	Ozaki (1969, 1972)
Nikenya, Mn mine, Tokushima Prefecture, Japan	Rdn, Cal	Ozaki (1969, 1972)
Kuranita, Akimoto mine, Miyazaki Prefecture, Japan	Qz, Ab, Cal, Brt	Ozaki (1969, 1972)
Akatore Creek, Eastern Otago, South Island, New Zealand.	Qz, Rdn, Pxm, “apatite”	Read & Reay (1971); Pringle & Kawachi (1980)
Vielle-Aure, Jurvielle and Tuc de Boup, Hautes-Pyrénées, France	Qz, Rdn, Rds, Py	Ragu (1990); De Ascencao Guedes <i>et al.</i> (2002)
Kyzyl-Tash deposit, Magnitogorsk area, southern Urals, Russia ¹	Qz, Rdn, Cal, parsettensite	Brunitsyn <i>et al.</i> (1997); Brunitsyn (2009)
Klučov near Třebíč, western Moravia, Czech Republic	Qz, Kfs, Cst	Škoda & Čopjaková (2005); Škoda <i>et al.</i> (2006)
<i>Reported localities lacking evidence for tinzenite</i>		
Nagakawara deposit, Ananai mine, Kochi Prefecture, Japan ²	—	Ozaki (1969, 1972); Minakawa <i>et al.</i> (2008)
Kozhayevskoye, Uchalinskoye and Urazovskoye Mn deposits, Magnitogorsk area, southern Urals, Russia ²	—	Barsanov (1951); Brunitsyn <i>et al.</i> (1997); Semkova & Brunitsyn (2002); Brunitsyn (2009)
Huachuca Mountains, Cochise County, Arizona, U.S.A. ^{2,3}	—	Milton <i>et al.</i> (1953); Lumpkin & Ribbe (1979); Anthony <i>et al.</i> (1995)
Diaspri <i>Auctt.</i> formation, Vagli, Apuan Alps, Lucca Province, Tuscany, Italy ²	—	Perchiazzi & Biagioni (2005)
Tanatz Alp, Spluga Pass, Grisons, Switzerland ⁴	—	Roth & Meisser (2011)

Note: ¹Two of 3 analyses give tinzenite, while 3rd gives axinite-(Mn), ²Analyses give axinite-(Mn), ³X-ray diffraction pattern gives axinite-(Mn) (Robert Downs and Marcus Origlieri, personal communication), ⁴No analytical data available. Mineral abbreviations: Ab – albite, Brt – barite, Cal – calcite, Cct – chalcocite, Cst – cassiterite, Hem – hematite, Hrm – harmotone, Py – pyrite, Pxm – pyroxmangite, Rds – rhodochrosite, Rdn – rhodonite.

solution between axinite-(Mn) and tinzenite. The proportion of the axinite-(Mn) + tinzenite end-members exceeds 75% in all cases and 90% in the samples poorest in Ca. Only one sample contained visibly less Ca than end-member tinzenite, and two samples had slight excess of Ca compared to axinite-(Mn). Eight analyses plot close to ideal tinzenite, 6 from Klučov near Třebíč, western Moravia, Czech Republic and two from Vielle-Aure, Jurvielle and Tuc de Boup, Hautes-Pyrénées, France (Table 1), one analysis from each locality is given in Table 2. FeO is the most abundant impurity (<1.5 wt%), and no other impurity exceeds 0.5 wt%.

4. Formula and definition of tinzenite

The revised formula, which is the same as that used in Back (2014), but rearranged and doubled to $\text{Ca}_2\text{Mn}_4^{2+}\text{Al}_4[\text{B}_2\text{Si}_8\text{O}_{30}](\text{OH})_2$ by analogy with formulae

for other axinite-group minerals in the IMA CNMNC list, meets the criteria given by Sanero & Gottardi (1968) for tinzenite and fulfils the requirements for proper end-member formulae (Hawthorne, 2002), which is not the case for the formula proposed by Belokoneva *et al.* (2001). In contrast to prediction based on crystallographic constraints that end-member tinzenite may not stable (Belokoneva *et al.*, 2001), the presence of near-end-member tinzenite from Klučov near Třebíč, Czech Republic (Škoda & Čopjaková, 2005; Škoda *et al.*, 2006) and from Jurvielle, Hautes-Pyrénées, France (Ragu, 1990) implies that end-member tinzenite is potentially stable if the necessary physical-chemical conditions are met.

Distinguishing tinzenite from axinite-(Mn) requires an analysis, either wet chemical or EMPA with an estimate of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (*e.g.*, from Fig. 1) and assuming stoichiometric H and B, and should be based exclusively on Ca content. The cutoff is Ca = 3 apfu, the midpoint between axinite-(Mn) and tinzenite (Fig. 2). Consequently,

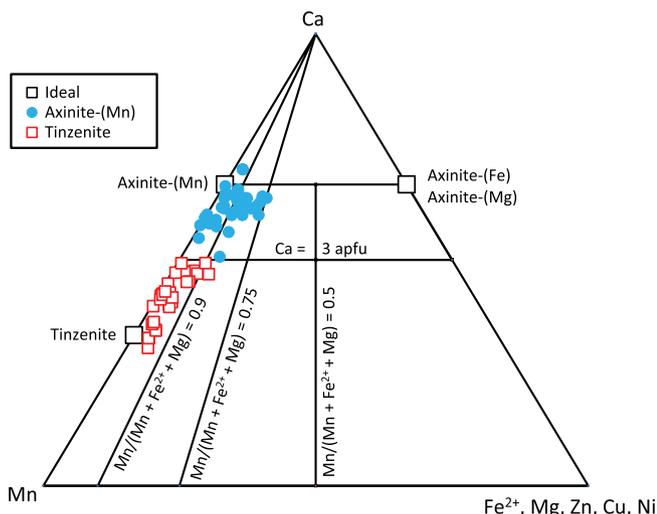


Fig. 2. Plot of 68 analyses of axinite-(Mn) and tinzenite containing >10 wt% MnO in terms of the atomic proportions of divalent cations (including Zn, Cu and Ni, which are much subordinate and reported by only a few authors). The plotted data include a formula reported by Perchiazzi & Biagioni (2005); other sources are the same as for Fig. 1.

the minerals reported as tinzenite from Huachuca, Arizona, USA and Lucca Province, Tuscany, Italy are axinite-(Mn) as are most of the Mn-rich axinites (“severginite” and “high-manganese severnigite”) from Magnitogorsk area, Southern Urals, Russia; only two compositions from Kyzyl-Tash plot in the tinzenite field (Table 2, Fig. 2).

5. Occurrence of tinzenite

Tinzenite has been confirmed from 10 localities; reports from an additional 4 localities have yet to be confirmed (Table 1). At 9 of these localities, tinzenite is found in veinlets (nests at Kyzyl-Tash) cutting stratiform manganese deposits composed of braunite, bementite, tephroite or rhodonite or metachert. Minerals associated with tinzenite in the veins are most commonly quartz, rhodonite, Mn-bearing calcite or rhodochrosite; parsetensite, bementite, sursassite, friedelite, barite, pyrite, pyroxmangite and feldspar are reported from a fewer number of localities. Minakawa *et al.* (2008) also reported epidote-(Sr) and tinzenite from the Nagakawara deposit in the Ananai mine, but did not give an analysis for tinzenite in this assemblage. Ozaki (1969, 1972) reported an analysis giving axinite-(Mn) from another assemblage in the Nagakawara deposit. The metamorphic conditions inferred for the manganese deposits range from the boundary between the pumpellyite-prehnite and pumpellyite-actinolite facies (Ananai mine, Kochi Prefecture, Japan, Minakawa *et al.*, 2008) through the pumpellyite-actinolite facies (Read & Reay, 1971; Pringle & Kawachi, 1980; Peters *et al.*, 1980; Tinizong, Switzerland; Akatore, New Zealand) up to low-grade, low-pressure greenschist facies (Hautes-Pyrénées, France, Cenki-Tok *et al.*, 2006), that is, up to about 300 °C (e.g., Spear, 1993, Fig. 2). Cenki-Tok *et al.* (2006) suggested that the tinzenite-

Table 2. Selected electron microprobe analyses of tinzenite close to the end-member in composition.

	Ideal	Ključov ¹	Jurvielle ²
<i>Weight%</i>			
SiO ₂	41.15	41.64	42.25
TiO ₂	–	0.00	0.00
SnO ₂	–	0.05	n.a.
Al ₂ O ₃	17.46	17.39	17.62
V ₂ O ₃	–	n.a.	0.49
Cr ₂ O ₃	–	n.a.	0.14
MgO	–	0.01	0.32
CaO	9.60	9.41	10.65
MnO	24.29	23.43	23.4
FeO	–	1.30	0.22
NiO	–	n.a.	0.01
CuO	–	0.13	n.a.
BaO	–	n.a.	0.00
Na ₂ O	–	0.02	0.00
K ₂ O	–	0.04	0.00
F	–	0.00	n.a.
S	–	n.a.	0.00
H ₂ O calc	1.54	1.56	1.59
B ₂ O ₃ calc	5.96	6.01	6.15
Sum	100.00	100.99	102.84
<i>Formula per 28 oxygen (excluding B and H)</i>			
Si	8	8.028	7.956
Al	4	3.951	3.911
V	–	–	0.073
Cr	–	–	0.021
Fe ³⁺	–	0.048	0.000
Sum	4	4.000	4.005
Fe ²⁺	–	0.161	0.035
Mn	4	3.826	3.732
Mg	–	0.003	0.090
Ca	2	1.944	2.149
Ni	–	–	0.002
Na	–	0.007	0.000
K	–	0.010	0.000
Cu	–	0.019	–
Sn	–	0.004	–
H calc	2	2.000	2.000
B calc	2	2.000	2.000
Total	22.000	22.001	21.968

Note: n.a. – not analyzed. Calc – calculated. Fe is reported as wt% FeO; Fe²⁺ = Fe_{tot} – (4 – Al – V – Cr) (see text). Sources for these electron microprobe analyses: ¹Near Třebíč, western Moravia, Czech Republic, Škoda *et al.* (2006); ²Hautes-Pyrénées, France, Ragu (1990). Weight % B₂O₃ and H₂O calculated from stoichiometry. V is assumed to be trivalent (Ragu, 1990, reported V as pentavalent).

bearing veinlets are most likely related to late hydrothermal fluids accompanying granitic cupolas, as other veinlets in the Hautes-Pyrénées deposits contain Be- and W-bearing phases. However, there is no evidence that veinlets at the other localities are related to granitic activity. It should be noted that these occurrences are not unique to tinzenite; axinite-(Mn) is also found in veinlets cutting manganese ore or metachert (Barsanov, 1951; Ozaki, 1969, 1972; Pringle & Kawachi, 1980).

The paragenesis of tinzenite at Klučov, Třebíč, Czech Republic is entirely different: a pegmatite of the niobium-yttrium-fluorine family, in which it occurs with quartz, K-feldspar and cassiterite filling a cavity in coarse-grained albite (Škoda & Čopjaková, 2005; Škoda *et al.*, 2006). Axinite-(Mn) is reported from miarolitic granitic pegmatites (Foord *et al.*, 1989; London *et al.*, 2012; Zagorsky *et al.*, 2016), a somewhat different paragenesis.

In summary, available information is not sufficient to explain the factors leading to formation of tinzenite *versus* axinite-(Mn). Nonetheless, conditions leading to crystallization of compositions approaching end-member tinzenite were attained both in manganese deposits (Ragu, 1990) and in granitic pegmatites (Škoda & Čopjaková, 2005; Škoda *et al.*, 2006).

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