

Special case of cation ordering in octahedral sites in natural epidote-supergroup minerals

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Crystals of natural dark green epidote from Sobotín, Czech Republic (ES) and natural brown-green clinozoisite from Baluchistan, Pakistan (CP) were studied for crystal-chemical variations before and after heating. Two samples from each other were not heat treated and were used as a standard while the eight other parts were heated in the muffle furnace in the air atmosphere for 12 hours and then cooled down to the ambient temperature for 12 h.

The average chemical composition of epidote in ES-0 – ES-9 is $\text{Ca}_{2.000}\text{Al}_{1.2.211}\text{Fe}_{0.742}\text{Si}_{2.994}\text{O}_{12}(\text{OH})$ and clinozoisite (CP-0 – CP-9) is $\text{Ca}_{2.017}\text{Al}_{1.2.626}\text{Fe}_{0.319}\text{Si}_{3.002}\text{O}_{12}(\text{OH})$. The main difference between samples is in Fe/Al ratio. Epidote from Sobotín is $M^3\text{Fe}^{3+}$ -dominant (0.68–0.80 apfu), while Fe^{3+} (between 0.29–0.33 apfu) is lower in clinozoisite samples. The content of other cations including Mg, Ti, V and Cr is very low or below the detection limit in both types of samples.

The unit-cell dimensions of both samples strongly depend on the Fe^{3+} -Al ratio. Original samples fall into the trend of epidote-clinozoisite solid solution very well with larger all a , b , c and V in Fe^{3+} -dominant epidote in ES sample compared to clinozoisite in CP. However, in heated samples, deviations from the trend can be observed. It is better pronounced in the CP samples with a vertical trend of increase in all a , b , c and V in heated samples. This trend could be partly attributed to small variations in Fe^{3+} -Al ratio but interestingly, sample heated at 900°C display significant increase in b . In contrast, the ES samples displays similar vertical trend only in c and partly in a ; variations in b and V have no significant vertical trend.

The position of Fe^{3+} in the epidote-clinozoisite structure can be read from the Mössbauer spectra; spectra of both sample sets heated below 1000°C contain doublets related to Fe^{3+} in octahedral coordination. However, there is a slight difference in doublets if both sample sets are compared. The ES spectra are symmetrical and can be interpreted as one doublet of Fe^{3+} in the $M3$ site. However, CP samples display slight asymmetry of Mössbauer spectra. This can be explained by presence of more components in spectra. First two components have isomer shift (IS) and quadrupole splitting (QS) typical for $M3$ site. Third doublet is close to Fe^{3+} in $M1$ site and takes area of 12-15 % corresponding to ca. 0.04 apfu in samples heated up to 500°C and increases up to 19 % (0.06 apfu) in samples heated at more than 500°C.

Incorporation of small amounts of Fe^{3+} in $M2$ can explain the presence of doublets with IS 0.31- 0.37 mm/s and QS 0.80-1.00 mm/s in the Mössbauer spectra of epidote-clinozoisite solid solution (Liescher, 2004). In our samples, doublets of the CP samples original and heated up to 800 °C have a similarly low QS but distinctly higher IS. Therefore, their interpretation as Fe^{3+} in $M2$ is not entirely clear but also not ruled out.

The $M1$ site links the oxygen atoms O1, O4, and O5. The O4–O5 edge is shared between individual octahedra forming chains to which the individual $M3$ octahedra are attached.

M1 and *M3* are connected by a common O1–O4 edge. The *M1* octahedron is fairly regular and its mean bond length is about 1.90 to 1.94 Å (Franz & Liebscher, 2004). Up to about $X_{Ep} = 0.6$ the *M1* octahedron exhibits only minor structural changes with increasing Fe content: the mean bond length, the volume, and the distance between the two apical O1 atoms slightly increase as response to the expansion of the attached *M3* due to increased Fe content on *M3* (Bonazzi & Menchetti, 1995).

Based on the site occupancy, attention must be paid to *M1* and *M3* octahedra, if the crystal chemistry of epidote-clinozoisite solid solution is going to be studied. The *M3* octahedron coordinates the oxygen atoms O1, O2, O4, and O8 and is the largest and most disorder site with the largest variability in occupancy (Ito et al., 1954; Stregiou et al., 1987; Grodzicki et al., 2001). Increasing Fe content increases its mean bond length from 1.98 to 2.06 Å (Franz & Liebscher, 2004). This mostly results from increase in the distance between the apical O4 and O8 due to the significant shift of O8; in clinozoisite it is considerable smaller than the comparable O1–O1 distance in *M1*, but increases significantly with increasing Fe content. Structural changes of *M3* are most pronounced for $X_{Ep} < 0.6$ and are in a clear linear relationship with Fe content. If X_{Ep} is higher than 0.6, the structural changes are less obvious and non-linear (Franz & Liebscher, 2004).

In the Mössbauer spectra, Fe^{3+} in *M1* is manifested by doublets with IS 0.22–0.36 mm/s and QS 1.46–1.67 mm/s (Bird et al., 1988; Fehr & Heuss-Assbichler, 1997; Heuss-Assbichler, 2000). Doublets in our CP-0 – CP-8 samples have slightly higher IS and QS but their interpretation as Fe^{3+} in *M1* is relatively reasonable. Moreover, Fehr & Heuss-Assbichler (1997) observed two doublets in the Mössbauer spectra that both displayed the main characteristics of Fe^{3+} on *M3* but with small differences in their QS. These were attributed to two slightly different *M3* sites, labelled *M3* and *M3'*, which belong to two different monoclinic epidote phases, one with Al- Fe^{3+} disorder on *M3* (*M3* doublet) and one with an ordered distribution of Al and Fe^{3+} at *M3* (*M3'* doublet); the latter represents the intermediate composition with $X_{Ep} = 0.5$ (Fehr & Heuss-Assbichler, 1997; Heuss-Assbichler, 2000).

However, this interpretation is relatively questionable, although, it can explain asymmetry of doublets in the CP samples very effectively. The Al- Fe^{3+} disorder between the *M1* and *M3* octahedral sites occurs at total Fe^{3+} contents higher than about $X_{Ep} = 0.6$ and is restricted to the *M1* and *M3* sites (Giuli et al., 1999). This obviously is not our case because CP clinozoisite contain only up to 0.3 Fe^{3+} apfu. On the other hand, variable degree of disorder in specific areas of clinozoisite structure may result not only in occurrence of probable *M1* doublet but also in above mentioned splitting of *M3* doublets which may be interpreted for instance as *M3* doublet for isolated $^{M3}Fe^{3+}$ and *M3'* doublet for the pair of $^{M1}Fe^{3+}$ and $^{M3'}Fe^{3+}$ in neighbouring octahedra.

Acknowledgments: This work was supported by the Ministry of Education of Slovak Republic grant agency under the contracts VEGA-1/0079/15 and VEGA-1/0499/16.

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