# Continuity in the monazite–huttonite series

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SUMMARY. Electron diffraction and electron-microprobe investigations have revealed the presence of order in the monazite-huttonite series. Chemical analyses from the literature and electron-microprobe analyses in this study show that the monazite-huttonite series, $REPO_4$–$ThSiO_4$, is only continuous if the contribution of F, $M^{2+}$, and OH to the charge balance is taken into account. The electron-diffraction study points to ordered domain structures in the series.

THORIUM is usually present in monazite in substitution for the rare earths from a few per cent up to at least 27 wt % (Frondel, 1958) but no correlation exists between Th and $RE$ (Murata, Rose, and Carron, 1953). Silicon can substitute for P in amounts up to 3 wt % (Frondel, 1958). Starynke-vitch (1922) found Th:Si ratio equalled 1:1 in monazite from Russian localities and accounted for it as a case of solid solution. However, in many other monazites Si is present but not in a 1:1 ratio with Th (Wylie, 1948; see also Frondel, 1958).

Huttonite, the other member of the series, was described as containing 0.8 wt % Fe, 2.5 wt % $RE$, and traces of P (Pabst, 1951).

Cheralite $(Th,Ca,Ce,La,U,Pb)[PO_4,SiO_4]$, the third isostructural compound belongs to the $REPO_4$–$CaTh(PO_4)_2$–$ThSiO_4$ ternary system (Bowie and Horne, 1953; Bowles, Jobbins, and Young, 1980).

The X-ray powder data (op. cit.) did not show the presence of superstructures and the chemical analysis cited were made using a large sample volume which precluded an exact control of homogeneity. For these two reasons monazite-huttonite grains were reinvestigated applying electron diffraction and electron-microprobe methods.

*Materials and methods of investigation.* Samples from Bogatynia area, Lower Silesia, Poland, were studied. They contain rock-forming minerals, niobium-bearing minerals (Banaś and Kucha, 1975), several Th minerals including cheralite, $FeTh(PO_4)_2$, thorogummite, Th-ningyoite (Kucha, 1979), huttonite-monazite, and their alteration products.

Minerals of the monazite-huttonite type form

grains up to 300 μm. The smallest are replaced by later Fe–Th mineralization. VHN of the mineral examined was (150 g load) $319 \pm 8$ kg/mm². 

Electron-microscope investigations were performed with an EF-4 Carl Zeiss microscope at 60 kV. Distances between diffraction spots were measured with an accuracy of $\pm 0.3$ mm. Particles for investigation were taken under a microscope from areas previously analysed using an electron microprobe and defined exactly to $10 \times 10$ μm.

The composition of the minerals was determined with an ARL SEMQ probe at 20 kV, sample current about 10 nA, using the following X-ray lines, synthetic compounds, and pure element standards: F-$K\alpha$($CaF_2$), Si-$K\alpha$, P-$K\alpha$($Ca_5F[PO_4]_3$), Ca-$K\alpha$($CaF_2$), Fe-$K\alpha$, $RE$-$L\alpha$ including Eu($L\beta_1$) and Gd($L\beta_1$) ($RE$ alloy), Pb-$L\alpha$, Th-$M\alpha$($ThO_2$), and U-$M\alpha$. Corrections to the X-ray data were applied for the absorption of radiation, fluorescence effects (Reed, 1965), and atomic-number differences (Philibert and Tixier, 1968). OH and $H_2O$ were calculated by difference and by balancing anions with cations.

*Electron-probe analyses.* The analyses of the minerals in question are reported in Table I. Three of them are of huttonite containing an admixture of rare earths (83/C1, C2, C6). Two have an undefined character (83/C4, C5). Judging from Th content they are huttonites, but the Si:P ratio near 1:1 puts them in the middle of the series. One analysis is of monazite with a high Th content.

The fact that both Th:Si and $RE$:P differ markedly from 1:1 shows that the simple coupled substitution $[Th^{+4}][Si^{+4}] \rightleftharpoons [RE^{+3}][P^{+5}]$ does not take place. Th:$[Si+F_4+(OH)_4]$ and $(RE+Ca)$:P ratios (Table I) are close to 1:1 and their sum is close to 2. This suggests that in monazite or huttonite when Th and $RE$ are substituted, the resultant valence differences are electro-statically compensated by the concomitant entrance of Ca, F, and $(OH)_4$. This seems to be closely connected with Th:$RE$ and Si:P ratios in the microarea of the lattice. The fact that the sum of Th:$[Si+F_4+(OH)_4]$ plus $(RE+Ca)$:P is close to 2

implies that the valence compensation in the lattice in the described case is realized practically without ion omissions.

Judging from the cation content the series is almost continuous—from the monazite end up to 27 wt% Th (Frondel, 1958) and up to at least 20 wt% of $RE$ from the huttonite end. This assertion is supported by X-ray scanning study showing that the distribution of $RE$ is undoubtedly heterogeneous. However, when considering the anion proportions, the series is continuous.

To summarize, chemical analyses already reported (op. cit.) and the microprobe analyses presented here provide evidence of substitution in the monoclinic $(RE,Th,M^{2+},U)[PO_4,SiO_4,OH,F]$ system close to $ThSiO_4$-$REPO_4$ boundary.

*Electron-diffraction analysis.* The order-disorder in the lattice of these minerals was investigated by means of an electron microscope which allowed a close comparison of microprobe and diffraction data. Fig. 1 shows an electron-diffraction pattern related to the composition 83/C4 (Table I). This electron-diffraction pattern is monoclinic with $a_0$ $6.61 \pm 0.06$, $b_0$ $7.19 \pm 0.07$, $c_0$ $6.32 \pm 0.06$ Å and

$\beta$ $101.8 \pm 1.2°$ similar to those of monazite and huttonite.

The most significant feature of fig. 1 is the presence of discrete satellite spots at fractional distances. It would probably be interpreted as the presence of small regions of order extending over several unit cells in size although the same effects are possible when the ordering consists of more than one original unit cell (Andrews, Dyson, and Keown, 1967).

The edges of the grains investigated were usually hydrothermally altered by the entrance of OH. Their electron-diffraction patterns showed stronger satellite spots. Thus entrance of OH would be an ordering factor probably due to the creating of monazite exsolutions, present mainly on the edge of the huttonite-monazite grains. However, electron-diffraction patterns from the edge of the grain had a far worse quality than presented in fig. 1.

Satellite reflections normally occur in pairs on either side of the main spots. However, in fig. 1, the satellites are present on one side of the main spot. Probably the pairs of satellites lie out of the
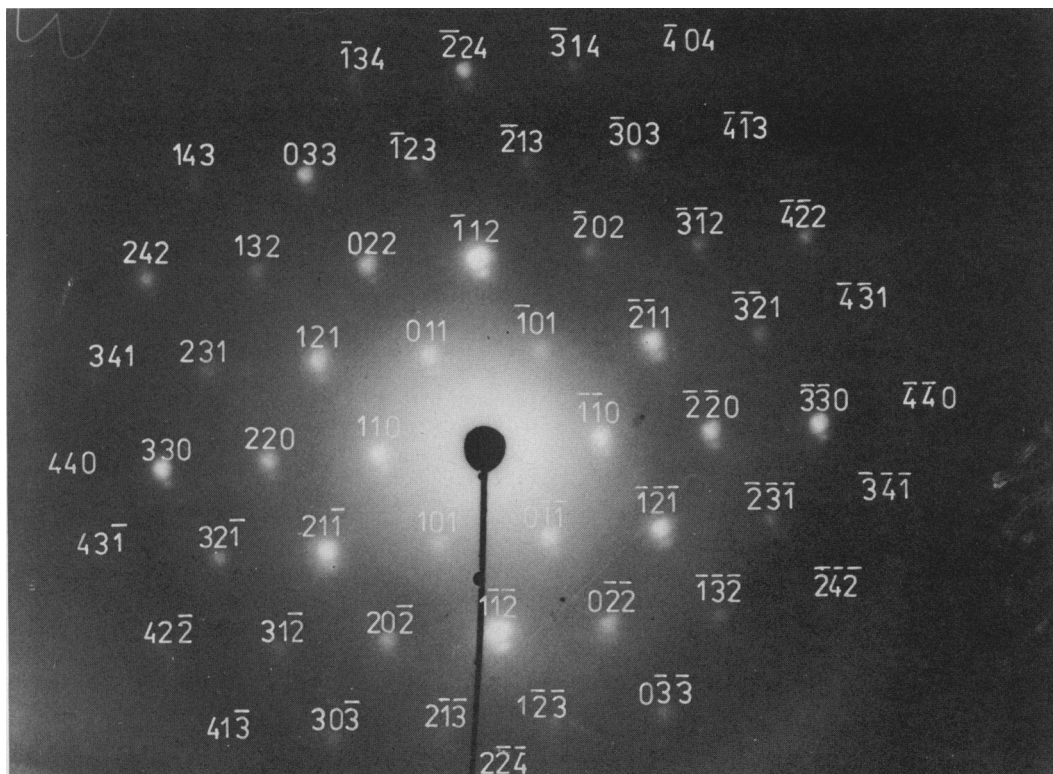


FIG. 1. Electron-diffraction pattern of mineral of the monazite huttonite series. Zone axis normal to the pattern [$\bar{1}1\bar{1}$]. Discrete satellite spots occurring near primary ones owe their presence to ordered domains in the monazite-huttonite series.

TABLE I. *Electron-probe analyses of minerals of huttonite–monazite series*

| | Weight %/Atomic proportions | | | | | | | | | | | Calc. | | Σ | Th:[Si+ F$_4$+(OH)$_4$] | (RE+ Ca):P | RE:P Th:Si |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | F | $SiO_2$ | $P_2O_5$ | CaO | FeO | $La_2O_3$ | $Ce_2O_3$ | $Pr_2O_3$ | $Nd_2O_3$ | $ThO_2$ | $UO_2$ | OH | $H_2O$ | | | | |
| 83/C1 | 1.0 | 13.5 | 7.1 | 1.8 | ≤0.5 | 2.1 | 6.2 | ≤0.15 | 3.6 | 64.0 | 0.8 | 0.5 | 0.0 | 101.1 | 1.00 | 1.14 | 0.750 |
| | 0.15 | 0.63 | 0.28 | 0.09 | 0.02 | 0.04 | 0.11 | | 0.06 | 0.68 | 0.01 | 0.08 | 0.00 | | | | 1.08 |
| 83/C2 | 1.5 | 10.4 | 8.9 | 1.3 | 0.5 | 2.0 | 7.6 | ,, | 4.0 | 63.6 | ≤0.45 | 1.93 | 0.0 | 101.7 | 1.07 | 0.92 | 0.667 |
| | 0.22 | 0.50 | 0.36 | 0.07 | 0.02 | 0.04 | 0.13 | | 0.07 | 0.68 | | 0.32 | 0.00 | | | | 1.36 |
| 83/C3* | 1.0 | 2.4 | 17.9 | 2.2 | ≤0.09 | 6.9 | 24.7 | 1.9 | 9.3 | 25.4 | ,, | 5.1 | 0.0 | 101.2 | 0.75 | 1.24 | 1.08 |
| | 0.12 | 0.10 | 0.63 | 0.10 | | 0.10 | 0.36 | 0.03 | 0.13 | 0.23 | | 0.71 | 0.00 | | | | 2.30 |
| 83/C4 | 2.0 | 8.1 | 11.2 | 1.3 | ,, | 4.0 | 14.6 | ≤0.15 | 1.9 | 56.4 | ,, | 2.6 | 0.0 | 102.1 | 1.06 | 0.93 | 0.795 |
| | 0.29 | 0.38 | 0.44 | 0.06 | | 0.07 | 0.25 | | 0.03 | 0.59 | | 0.43 | 0.00 | | | | 1.55 |
| 83/C5 | 0.8 | 11.1 | 10.5 | 1.7 | 0.4 | 2.7 | 9.8 | 0.7 | 3.5 | 58.3 | ,, | 0.7 | 0.6 | 100.8 | 1.06 | 0.93 | 0.707 |
| | 0.12 | 0.51 | 0.41 | 0.08 | 0.01 | 0.05 | 0.17 | 0.01 | 0.06 | 0.62 | | 0.11 | 0.08 | | | | 1.22 |
| 83/C6 | 1.0 | 12.8 | 7.1 | 2.5 | ≤0.09 | 0.9 | 2.7 | ≤0.15 | 0.9 | 69.9 | 1.0 | 1.8 | 0.0 | 100.6 | 1.06 | 1.00 | 0.409 |
| | 0.16 | 0.63 | 0.22 | 0.13 | | 0.02 | 0.05 | | 0.02 | 0.78 | 0.01 | 0.31 | 0.00 | | | | 1.24 |

≤—Limit of microprobe detection.
*—Contains also (wt %): $Sm_2O_3$ 2.3 (0.03 at.), $Eu_2O_3$ 1.2 (0.02 at.), and $Gd_2O_3$ 0.9 (0.01 at.).

plane of the diffraction pattern. The finite curvature of the reflecting sphere, significant for 60 kV electrons, causes only one of each pair of satellites to be observed (see Andrews *et al.*, 1967).

*Conclusions.* The monazite–huttonite series is continuous at the monazite end to at least 27 wt % of Th and from the huttonite end to at least 20 wt % of *RE*. Substitution of $PO_4$ for $SiO_4$ is continuous but not in the pure $REPO_4$–$ThSiO_4$ system. It includes additionally F, $M^{2+}$, and OH.

The electron-diffraction data showed ordered domains on a scale too fine to be resolved by means of a microprobe beam and for this reason they are not inconsistent with the microprobe results.

The data indicates also that there is no mineralogical reason to distinguish any new, intermediate, monoclinic phase in the ternary $RE[PO_4]$–$CaTh[PO_4]_2$–$ThSiO_4$ field given by Bowie and Horne (1953).

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