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The iron content and the optic axial angle in zoisites from Galicia, NW Spain

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ABSTRACT. Electron probe microanalyses of zoisites from high-grade metamorphic rocks in Galicia, NW Spain have been obtained. The elements Na, Mg, P, K, Ti, and Mn were not detected above the 0.1 wt. % level. Assuming all Fe is present as Fe^{3+}, a clear relation is obtained between the Fe content and the optic axial angle. Zoisite with 1.6 wt. % Fe_2O_3 proves to be uniaxial at 589 nm; uniaxiality in blue light (470 nm) lies at 1.5 wt. % Fe_2O_3. A change of the optic sign, from positive to negative, is obtained at 2.9 wt. % Fe_2O_3. The presence of minor elements greatly affects this relation, as is indicated by analyses of sector-zoned Sr-bearing zoisites of a muscovite–zoisite pegmatite from the same region. Under retrograde conditions Fe-rich α-zoisite reacts to form less Fe-rich α-zoisite or β-zoisite and clinozoisite.

KEYWORDS: zoisite, metamorphism, optic axial angle, iron, Galicia, Spain.

THE existence of two types of zoisite with different optical orientations was first recognized by Termier (1898, 1900). The two types are named α-zoisite and β-zoisite after the vibration direction which lies parallel to the crystallographic *b*-axis, along which zoisite is usually prismatically developed. α-zoisite has α, β, and γ parallel to *b*, *a*, and *c*, respectively; OAP parallel to (100), varying $2V_\gamma$ and strong rhombic dispersion $r \ll v$. β-zoisite has α, β, and γ parallel to *a*, *b*, and *c*, respectively; OAP parallel to (010) and perpendicular to the cleavage (100), varying $2V_\gamma$ and rhombic dispersion $r > v$.

These data are usually given in literature on zoisite mineralogy and in determinative tables (Myer, 1966; Saggerson, 1975; Tröger, 1982). Deer *et al.* (1967) and Battey (1975) give a reverse dispersion scheme for both α- and β-zoisites. Vogel and Bahezre (1965) note the existence of a zoisite with a large $2V_\alpha$ with rhombic dispersion $r \gg v$.

The connection between the two types of zoisite and their ferric iron content has been much debated (Phillips and Griffen, 1981; Saggerson, 1975; Termier, 1900; Winchell and Winchell, 1959). A relation, which nowadays is generally accepted has been given by Myer (1966), with later confirmation by Enami and Banno (1977). Myer analysed five non-manganiferous zoisites and measured the optic axial angle $2V_\gamma$ in Na_D light; his data are given in fig. 1.

α-zoisite is generally considered to be the high-temperature zoisite, occurring as a primary mineral in eclogitic rocks of various compositions, whereas during retrograde metamorphism β-zoisite forms (Raith, 1976; Richter, 1973; Vogel, 1967).

The present study was undertaken to refine the extrapolated curves of Myer and of Enami and Banno. Seventeen zoisite-bearing samples were collected from Cabo Ortegal, Galicia, NW Spain. α-zoisite occurs as a stable phase, together with omphacite, garnet and brownish pargasitic hornblende in α-zoisite eclogites, α-zoisite hornblende eclogite and α-zoisite hornblende pyrigarnites. The primary metamorphic character of the mineral may be deduced from the fact that it occurs as inclusions in omphacite and garnet; moreover, the minerals sparsely included in α-zoisite are of primary nature, e.g. rutile and garnet (Vogel, 1967).

The formation of kelyphitic rims around garnet and the replacement of omphacite by common hornblende mark the first stages of alteration of the eclogites into amphibolites. The growth of β-zoisite occurs during this retrogressive phase. The iron released by α-zoisite breakdown will be easily redistributed among other minerals, such as garnet and hornblende, at lower metamorphic conditions.

In these retrograde rocks both zoisite varieties may be found within one sample: individual grains with compositions within the α-zoisite or β-zoisite compositional range, individual grains with compositions across the α-β zoisite boundary (α-zoisite cores with β-zoisite rims, lamellar intergrowths of α-zoisite and β-zoisite).

Optically negative α-zoisite occurs in post-eclogitic pegmatoid veins (sample G 7-2) and as rather irregular patches within α-zoisite in the α-zoisite hornblende pyrigarnite (sample M 643); see also fig. 2*a* and *b*. These patches are easily recognized by different anomalous interference colours.

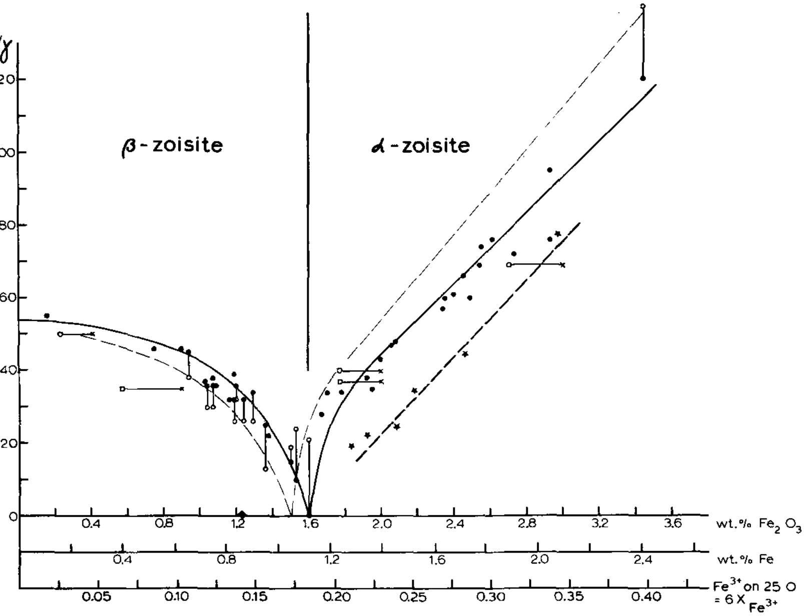

FIG. 1. The relation between the iron content and the optic axial angle in zoisites. Closed circles, this study (at 589 nm), full line; open circles, this study (at 470 nm), dashed line; asterisks, Sr-bearing zoisites, this study (at 589 nm); rectangles, Myer (1966); crosses, Myer (1966), all iron assumed to be trivalent; diamond, transition point of Myer (1966). Note: $X_{Fe^{3+}} = X_{Fe^{3+}}/(X_{Fe^{3+}} + Al)$.

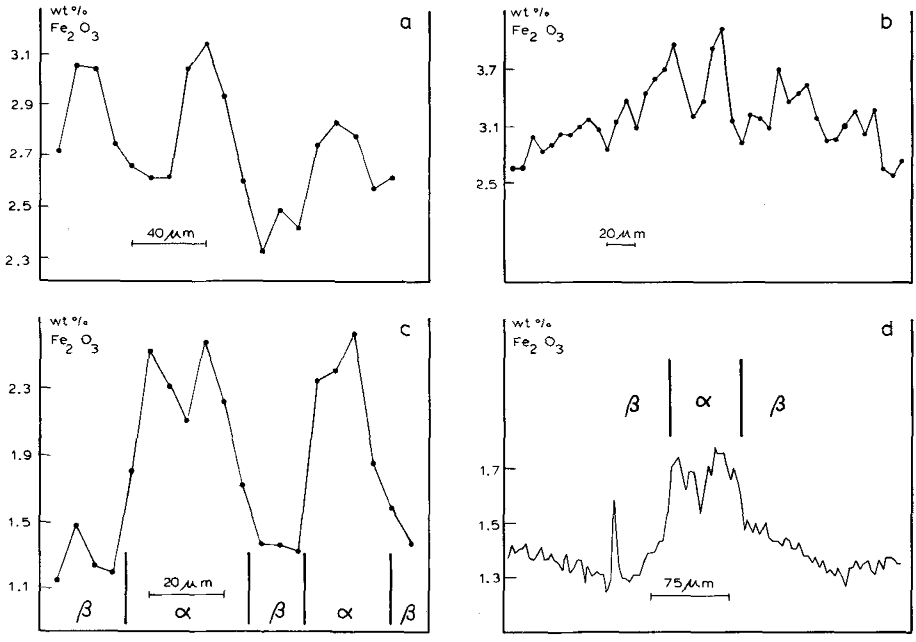

FIG. 2. Step scans for Fe-$K\alpha$ across zoned zoisite grains. (*a*) α-zoisite (> 2.9 wt. % Fe_2O_3) patches within α-zoisite (sample M 643); (*b*) fluctuations in optically negative α-zoisite composition (sample M 643); (*c*) lamellar intergrowth of α- and β-zoisite (sample Ma 13); (*d*) α-zoisite core within β-zoisite (sample Ma 13).

Analytical procedures. Electron probe microanalyses were carried out on a Cambridge Instruments Microscan 9 with an on-line ZAF program after Sweatman and Long (1969). In each polished thin section, 8 to 10 zoisite grains were selected for analysis. Selection criteria were grain size, clearness, optical homogeneity and low birefringence, to facilitate optic axial angle measurements on the universal stage. Synthetic åkermanite and gehlenite were used as standards for Ca, Si, and Al (Ii and Shindo, 1979). St John's Island olivine was taken as a standard for Fe.

Spot analyses were carried out at 15 kV accelerating potential, 50 nA specimen current on a Faraday cage and 40 sec integrating time.

Under these conditions, counting statistics give 2σ values for individual Fe measurements of about 3 % at the 2 wt. % Fe level and of about 0.5 % for Al, Si, and Ca. Step scans were made across zoned grains. The variation in Fe content was usually double-checked by setting the LiF analysing crystals in both spectrometers at the Fe-$K\alpha$ peak.

Optic axial angle measurements were obtained on a Zeiss five-axial universal stage on analysed zoisite grains. Monochromatic light was obtained with a Schott continuous-running filter, type Veril B-200, whose half-width at half-height is 25 nm at 589 nm and 30 nm at 470 nm. Measurements were made at 589 nm (comparable with Na_D light) and, less frequently, at 470 nm (blue light).

Analytical results. Fig. 1 gives the relation between the Fe content and the optic axial angle in the analysed zoisites. Tables with complete electron probe data and optic measurements are available on request.

The figure shows: (*a*) a shift of the transition, from β-zoisite to α-zoisite, from about 1.2 wt. % Fe_2O_3 (Myer, 1966) to 1.6 wt. % Fe_2O_3, corresponding with $X_{Fe} = 0.03$ (Enami and Banno, 1977); (*b*) distinctly lower optic axial angles in a sector-zoned Sr-bearing zoisite, in a zoisite–muscovite pegmatite from the same region, with SrO 1.2, P_2O_5 0.3, and Cl 0.1 wt. %, indicating the influence of the presence of minor elements on the size of the optic axial angle; (*c*) the clear relation between high Fe contents and the optically negative character of the α-zoisite (at > 2.9 wt. % Fe_2O_3).

Variations in the Fe content of the analysed zoisite grains within one sample may be due to (*a*) compositional differences between zoisite grains of the same generation, (*b*) stable or metastable coexistence of relatively Fe-poor and Fe-rich zoisite populations, (*c*) zoned zoisite grains, caused by gradational and/or step-like transition from relatively Fe-rich to Fe-poor compositions upon retrograde metamorphism, and (*d*) statistical variations.

All iron is assumed to be present as Fe^{3+}. This assumption seems warranted in view of the clearly antipathetic relationship between wt. % Fe_2O_3 and wt. % Al_2O_3. The elements Na, Mg, K, Ti, and Mn are not present above the 0.1 wt. % level.

The transition from β-zoisite to α-zoisite and the corresponding change in the optical orientation could be clearly analysed in a zoned zoisite grain in sample Ma 13. A scanning profile for Fe-$K\alpha$ radiation across this grain is given in fig. 2*d*. Fig. 2*c* shows a stepscan for Fe-$K\alpha$ radiation across lamellar intergrowths of α-zoisite and β-zoisite in the same sample. Both figures demonstrate a relatively steep compositional gradient across the α-β-zoisite transition.

Zoisite-clinozoisite relations. Coexisting zoisite and clinozoisite have been reported by many authors (Banno, 1964; Myer, 1966; Ackermand and Raase, 1973; Hietanen, 1974; Raith, 1976; Enami and Banno, 1980). The stability relations between the two minerals are, however, not fully understood. Most authors favour a shift of the compositional gap between zoisite and clinozoisite towards the Fe^{3+}-rich region with an increase of temperature.

Enami and Banno (1980) studied several zoisite–clinozoisite-bearing rocks (albite-epidote amphibolites, epidote amphibolites, metagabbros) from

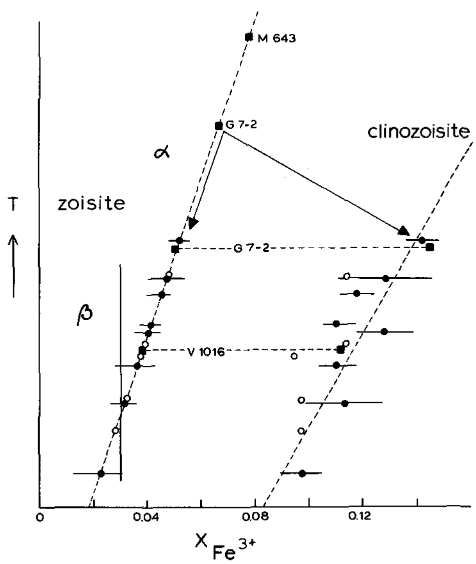

FIG. 3. Speculative temperature–composition relation for the zoisite–clinozoisite series (after Enami and Banno, 1980). The transition loop is approximated by straight lines, and the relative formation temperatures were inferred from $X_{Fe^{3+}}$. Closed circles, Enami and Banno, 1980; open circles, Ackermand and Raase, 1973; rectangles, this study.

Japan. They established a speculative phase diagram of the zoisite–clinozoisite system at temperatures of low- to medium-grade metamorphism: from greenschist to epidote–amphibolite facies. Coexisting zoisite and clinozoisite also occur in some high-grade metamorphic rocks from this study. In a quartz-zoisite vein in a garnet amphibolite, a retrogressive eclogite (sample G 7-2), large primary α-zoisite grains are at their rims replaced by less Fe-rich α-zoisite and clinozoisite. The growth of individual clinozoisite grains in a kelyphitized α-zoisite eclogite may be observed in sample V 1016.

The chemical composition of these coexisting phases is plotted in fig. 3, the inferred phase diagram of Enami and Banno (1980), together with data given by Ackermand and Raase (1973). All zoisite data are plotted on a straight line, in accordance with the procedure followed by Enami and Banno (1980).

With these data the evidence in favour of a compositional gap between coexisting zoisite and clinozoisite, which shifts to Fe-richer compositions at higher temperatures, is strengthened.

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