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Oscillatory zoned chrome lawsonite in the Tavşanlı Zone, northwest Turkey

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ABSTRACT

Blueschist-facies metabasite rocks from the Tavşanlı Zone of northwest Turkey have been found to contain an abundance of lawsonite displaying oscillatory zoning. Lawsonite normally adheres to the ideal composition of $CaAl_2[Si_2O_7](OH)_2.H_2O$. In two samples from the Tavşanlı Zone, Al^{3+}-Cr^{3+} substitution has occurred. The Cr^{3+} was probably present in the protolith as magmatic chromite, became incorporated into lawsonite during subduction, and is a metamorphic feature resulting from quantities of Cr in the protolith and local fluid conditions.

Keywords: lawsonite, oscillatory zoning, metamorphic rocks, Tavşanlı zone, Turkey.

Introduction

Lawsonite is a mineral found within a variety of metavolcanic and metasedimentary lithologies that have undergone high-pressure low-temperature (*HP-LT*) conditions of metamorphism. Recent experiments have shown that lawsonite is stable to 120 kbar and 960°C, and occurs in the subducting slab (Schmidt, 1995). The general structure of lawsonite as $CaAl_2[Si_2O_7](OH)_2.H_2O$ was first determined by Wickmann (1947), and later redefined by Bauer (1978). Lawsonite rarely deviates from the ideal composition, and experiences no changes in the lattice structure during subduction (Comodi and Zanazzi, 1996). To our knowledge there is only one other reported occurrence of chromium lawsonite, within a Cr-rich metagabbro in the Piemont zone, western Alps (Mevel and Kienast, 1980). Within the Tavşanlı Zone of northwest Turkey, oscillatory zoned lawsonite occurs within blueschist-facies metabasites from a small region of high-pressure low-temperature (*HP-LT*) rocks.

The aim of this paper is to describe a first occurrence of Cr in lawsonite from the Tavşanlı Zone in northwest Turkey, and more importantly the first occurrence of oscillatory zoning recorded in lawsonite. Oscillatory zoning is a relatively common feature observed in magmatic, metamorphic, hydrothermal and diagenetic minerals and may be the result of either environmental fluctuations during near-equilibrium growth, or from non-equilibrium growth. In the case of magmatic minerals such as pyroxene or feldspar, differences in pressure, temperature or chemical composition in a convecting magma chamber or solution may be invoked (e.g. Bowen, 1928).

Occurrences of oscillatory zoning in metamorphic minerals

Oscillatory zoning in metamorphic minerals is less common than in igneous minerals, and previously recorded occurrences are summarized in Table 1. With the exception of plagioclase, all have developed oscillatory zoning in response to fluctuations in either fluid supply or fluid composition. Epidote and prehnite from an active geothermal field grew during rapidly fluctuating

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TABLE 1. Known occurrences of oscillatory zoned metamorphic minerals

Mineral	Location/tectonic setting	Reference
Prehnite and epidote	Active geothermal field, Costa Rica	Yardley *et al.* (1991)
Pyroxene	Fraser Mine, Australia	Yardley *et al.* (1991)
Pyroxene	Connemara marble	Yardley *et al.* (1991)
Garnet	Skarn deposit, Norway	Jamtveit, 1991; Jamtveit *et al.* (1993)
Plagioclase	Calc-pelite schist, Vermont	Menard and Spear (1996)

redox conditions and $a_{Fe^{3+}}$ oscillations (Yardley *et al.*, 1991). Pyroxenes from Fraser Mine grew under conditions of both fluctuating fluid composition and fluid influx rate, and pyroxenes in the Connemara marble developed oscillatory zoning due to the interaction of quartz-saturated fluid with dolomite (Yardley *et al.*, 1991). Garnets in skarn deposits grew in a contact metamorphic environment, due to both complex epitaxial growth and changing fluid conditions (Jamtveit, 1991; Jamtveit *et al.*, 1993). In contrast, the oscillatory zoning in plagioclase is not entirely attributed to changing fluid conditions, but is due, in part, to plagioclase overgrowing a heterogeneous matrix of crenulated muscovite (Menard and Spear, 1996).

Geological setting

The lawsonites described here are found within the Tavşanlı Zone of northwest Turkey. The Tavşanlı Zone is an east−west trending linear tract of *HP-LT* rocks, lying south of the major Izmir-Ankara suture (Fig. 1). The suture is one of many found within the Alpine-Himalayan orogenic chain and represents the site of a major northeast-directed oblique subduction zone responsible for the consumption of the Tethys Ocean during the Cretaceous (Okay, 1989). The Tavşanlı Zone comprises sedimentary and volcanic rocks, which have been metamorphosed in the blueschist- and low-temperature eclogite-facies, and are subducted remnants of the passive continental margin of the Anatolide-Tauride platform. White mica Rb-Sr ages for the subduction-related *HP-LT* metamorphic event are ~80 Ma (Sherlock *et al.*, 1999), pressures and temperatures of metamorphism are estimated to be in the region of 24 kbar and 400 to 450°C (Sherlock *et al.,* in prep.).

Within the Halilbagi region in the east of the Tavşanlı Zone (Fig. 1) there is a small region of intercalated marble, metachert, foliated metabasites, metapelites and poorly foliated porphyroblastic metabasites that have undergone *HP-LT* metamorphism, from which metabasic lithologies with a volcanic protolith have been collected, and it is these which contain the unusual oscillatory zoned Cr-lawsonite.

Sample descriptions

Samples 96/152 and 96/67 are foliated metabasites with the assemblage lawsonite ± clinopyroxene ± sodic amphibole + white mica + apatite + calcite + chlorite ± titanite + talc. Within sample 96/152, pre-kinematic lawsonites and clinopyroxenes are sub-idioblastic and reach a maximum diameter of 500 μm, white mica and a second clinopyroxene are finer grained and form the dominant fabric which wraps around the lawsonite and clinopyroxene grains. Apatite is a common accessory mineral, and there is evidence of late alteration in the form of fine-grained chlorite, talc and calcite. Sample 96/67 is a compositionally banded metabasite, with bands rich in sub-idioblastic lawsonite of up to 300 μm in diameter, and fine-grained sodic amphibole and white mica. Titanite is a common accessory phase and fine-grained talc is a late alteration product.

Average chemical analyses are presented in Table 2, and have been determined using a Cameca SX100 electronprobe microanalyser at The Open University, with a 20 kV accelerating voltage, 20 nA beam current and a spot size of 10 μm.

Mineral chemistry

Amphiboles in sample 96/67 reach a maximum of 150 μm in diameter and are both optically and chemically zoned. Average compositions are glaucophane and are chrome-free; grains have lilac blue cores and dark blue rims corresponding to glaucophane-rich cores and ferroglaucophane

FIG. 1. Location map of the major tectonic units in Turkey, highlighting the Tavşanlı Zone and Halilbagi, the sources of samples 96/69 and 96/152, respectively.

rims after the amphibole classification of Leake *et al.*, (1997). The Fe^{3+} in amphibole has been determined according to the recalculation method of Okay (1980*b*). The core-rim optical zoning observed in amphiboles corresponds to decreasing Mg^{2+} and increasing Fe^{2+} from core to rim, with an overall decrease in Al^{3+} and corresponding increase in Fe^{3+}. In sample 96/152, the pre-kinematic sub-idioblastic clinopyroxenes are more augitic and with a jadeite component of $Jd_{(21)}$, whilst later syn-kinematic clinopyroxenes are much finer grained, less augitic and with a higher jadeite component of $Jd_{(23)}$. Both clinopyroxene generations contain Cr; pre-kinematic grains contain an average of 0.30 wt.%, whereas syn- to post-kinematic grains have a lower concentration of 0.19 wt.%. Syn- to post-kinematic white micas, which are aligned with the main foliation are phengitic, with average Si = 3.70 and 3.58 in samples 96/152 and 96/67 respectively. Micas in sample 96/152 do not contain measurable Cr, whereas micas in sample 96/67 on average contain 0.3 wt.%.

Chrome lawsonite

Lawsonites are idioblastic to sub-idioblastic squat prismatic grains, compositionally ideal with the exception of the presence of Cr^{3+}. On average, sample 96/67 has twice the amount of Cr – 6.40 wt.% – compared with 3.62 wt.% in sample 96/152. In both samples, Cr^{3+} is oscillatory zoned and varies antithetically with Al (Fig. 2).

In both samples the oscillatory zoning is concentric. In sample 96/67, the cores are oscillatory zoned with a monotonically zoned outer margin (Fig. 3*a*). In sample 96/152, oscillatory zoning in lawsonite persists from core to rim (Fig. 3*b*). In both cases Cr^{3+} and Al^{3+} co-fluctuate on a sub-10 μm level. There are no further compositional variations; lawsonite is either ideal or it contains Cr^{3+}.

TABLE 2. Representative chemical analyses of minerals from samples 96/152 and 96/67

	Amphibole	Clinopyroxene		Lawsonite		Mica		Talc	
	67	152 (1)	152 (2)	152	67	152	67	152	67
SiO_2	56.65	54.79	54.36	37.05	39.30	57.33	52.65	60.15	61.78
Al_2O_3	5.83	4.83	5.40	26.25	25.00	14.83	21.82	0.70	0.68
Cr_2O_3	0.00	0.33	0.19	3.62	6.40	0.07	0.30	0.04	0.01
Fe_2O_3	7.48	7.52	9.36	0.00	0.00	0.00	0.00	0.00	0.00
FeO	13.3	3.52	2.04	1.41	1.90	4.80	3.86	6.13	6.83
MnO	0.29	0.18	0.16	0.04	0.03	0.03	0.04	0.05	0.14
MgO	7.74	9.87	8.50	0.00	0.03	13.52	4.81	24.77	27.22
CaO	0.68	12.39	13.40	16.72	16.90	0.00	0.02	1.73	0.03
Na_2O	6.20	6.13	6.57	0.03	0.01	0.22	0.08	0.59	0.03
K_2O	0.04	0.01	0.00	0.00	0.01	6.73	10.86	0.03	0.01
Total	98.27	99.48	99.98	87.97	89.72	97.50	94.44	94.11	96.73
Si	8.05	2.01	1.99	3.20	3.27	3.70	3.58	7.96	7.94
Al	0.98	0.21	0.23	2.67	2.44	1.15	1.75	0.11	0.11
Cr	0.00	0.01	0.01	0.25	0.43	0.00	0.02	0.01	0.00
Fe^{3+}	0.81	0.21	0.26	0.00	0.00	0.00	0.00	0.00	0.00
Fe^{2+}	1.58	0.11	0.06	0.10	0.14	0.13	0.22	0.68	0.73
Mn	0.04	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.02
Mg	1.04	0.54	0.46	0.00	0.00	1.32	0.48	4.89	5.21
Ca	0.10	0.48	0.52	1.43	1.50	0.00	0.00	0.25	0.01
Na	1.71	0.44	0.47	0.00	0.00	0.03	0.01	0.15	0.01
K	0.00	0.00	0.00	0.00	0.00	0.57	0.94	0.01	0.00
Total	14.90	4.00	4.01	7.65	7.78	6.91	6.92	14.07	14.01
Jd		21	23						
Ac		23	24						
Aug		56	53						

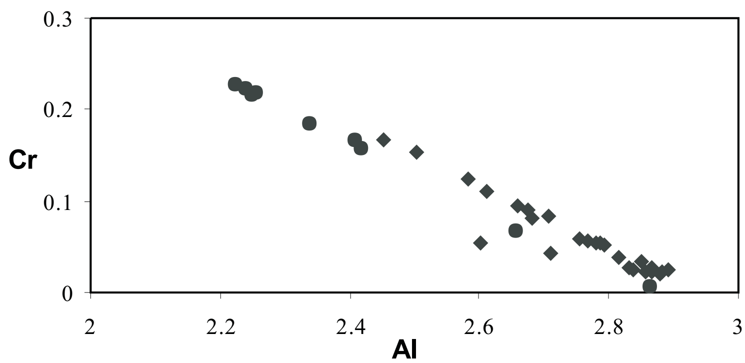

FIG. 2. Al^{3+}/Cr^{3+} substitution diagram plotted for lawsonites from samples 96/69 (circles) and 96/152 (squares).

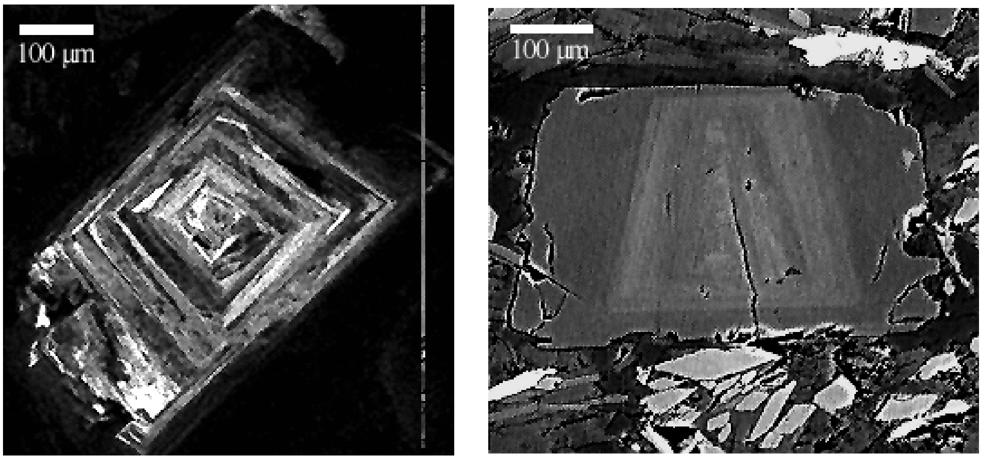

FIG. 3. Images of oscillatory Cr^{3+}/Al^{3+} zoning in lawsonite in: (*a*) X-ray map of Cr, sample 96/67; and (*b*) backscattered electron image, sample 96/152.

Discussion

Within the Tavşanlı Zone the only lawsonites which are oscillatory zoned are those within metabasites characterized by a high bulk Cr_2O_3. The pre-kinematic pyroxenes were originally igneous, and were topotactically replaced during static recrystallization in the subducting slab (Okay, 1980*a*). The Cr^{3+} may have been present in the original igneous pyroxene, though more likely within magmatic chromite. Pre-kinematic lawsonite is inferred to have been formed during the same static event during subduction. Since coexisting phases show no significant zoning, the oscillatory zoning in lawsonite is unlikely to be the result of rapidly changing externally controlled parameters such as pressure and temperature. Detailed *PT* analyses suggest that steady-state conditions prevailed during subduction (Sherlock *et al.,* in prep.) which preclude any rapid or fluctuating changes in temperature and pressure as a possible mechanism. In this case the Cr in lawsonite will have originated from chromite grains in the protolith, with the oscillatory zoning resulting from fluid/rock interaction.

Fluids originating from the subduction and consequent dehydration of sediments and volcanics may well have interacted with lawsonite during growth. In particular Cr^{3+} originated from chromites within the volcanic protoliths, which then substituted for Al^{3+} in lawsonite. The oscillatory nature of the zoning may have been achieved through local fluid buffering by chromite grains and slow equilibration at the fluid-crystal interface. A second mechanism may be a result of fluctuating f_{O_2}. Oxygen fugacity is a locally buffered component (e.g. Chinner, 1960; Greenwood, 1975). Previous studies in the Tavşanlı Zone illustrate that changing f_{O_2} modifies the Fe^{2+}/Fe^{3+} ratio in the sodic amphiboles (Okay, 1980*b*), producing similar compositional zoning to that observed in amphiboles in sample 96/67, indicative of reduction during amphibole growth. It may be possible that the Cr^{2+}/Cr^{3+} is similarly affected and whilst the fluid is oxidizing the Cr^{3+}/Al^{3+}, substitution is facilitated in lawsonite. An alternative is that if chromite grains were present within the igneous protolith matrix they may have been shielded by surrounding matrix minerals and only mobilized sporadically when the shield was broken. This however makes the assumption that chromite was present within the matrix, of which there is now no evidence.

Syn-kinematic phengites in sample 96/67 and clinopyroxene in sample 96/152 contain minor quantities of Cr^{3+} which may be a result of later remobilization of Cr^{3+} during the higher temperatures following peak-pressure conditions, and associated with the onset of exhumation.

Conclusions

The first recorded occurrence of oscillatory zoning in lawsonite occurs in metabasite lithologies from the Halilbagi region of the Tavşanlı Zone in northwest Turkey. Cr^{3+}/Al^{3+} substitution is responsible for the zoning. Fluids which probably originate from the dehydration of subducting sediments and volcanic rocks are either buffered locally by chromite in the volcanic protolith, or changes in f_{O_2} which have already been described in the Tavşanlı Zone (Okay, 1980*b*) may be responsible for fluctuations in $a_{Cr^{3+}}$. Sodic pyroxenes which formed topotactically from pre-existing magmatic pyroxenes do not display oscillatory zoning, it has been suggested that hydrous phases such as amphibole and in this case lawsonite, are more highly susceptible to f_{O_2} fluctuations than anhydrous phases such as pyroxene (Okay, 1980*b*). Adjacent lawsonite-bearing metachert and metapelite lithologies contain neither Cr^{3+} or oscillatory zoned lawsonites. It is suggested that oscillatory zoning in lawsonite is a primary metamorphic feature culminating from quantities of Cr^{3+} in the protolith and local fluid conditions.

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