

OXYGEN ISOTOPE DATA ON THE FORMATION TEMPERATURE AND ORIGIN OF A SLIP-FIBER CHRYSOTILE ASBESTOS DEPOSIT, ZIDANI, NORTHERN GREECE

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ABSTRACT

Oxygen isotope compositions have been determined for the Zidani slip-fiber chrysotile asbestos deposit. The restricted range of $\delta^{18}\text{O}$ of serpentine and magnetite indicates that probably only small amounts of fluid were involved during the alteration of antigorite serpentinite to chrysotile asbestos fibers. The serpentine-magnetite geothermometer suggests temperatures of 400-450°C, which are assigned to the antigorite formation event. The calculated $\delta^{18}\text{O}$ of the waters are metamorphic values.

ΣΥΝΟΨΗ

Στο κοίτασμα χρυσοτιλικού αμιάντου (τύπου slip-fiber) του Ζιδανίου υπολογίστηκε η ισοτοπική σύσταση του οξυγόνου. Η μικρή διασπορά των $\delta^{18}\text{O}$ τιμών του σερπεντίνης και του μαγνητίτη δείχνει ότι μόνο μικρές ποσότητες ρευστού κυκλοφόρησαν κατά την εξαλλοίωση των αντιγοριτικών σερπεντινιτών σε ίνες χρυσοτιλικού αμιάντου. Από το γεωθερμόμετρο σερπεντίνη-μαγνητίτη υπολογίστηκε θερμοκρασία 400-450°C, η οποία αντιπροσωπεύει την θερμοκρασία σχηματισμού του αντιγορίτη. Οι υπολογιζόμενες $\delta^{18}\text{O}$ τιμές θεωρούνται τιμές μεταμορφικών ρευστών.

INTRODUCTION

Chrysotile asbestos deposits are related to a specific stage of the serpentinization process. The transition of lizardite pseudomorphic textures to lizardite hourglass and lizardite \pm chrysotile \pm antigorite interlocking textures is characteristic of chrysotile asbestos deposits (O'Hanley 1991).

Investigations of the stable isotope compositions of serpentine minerals by Wenner and Taylor (1971, 1973, 1974), Magaritz and Taylor (1974), and Ikin and Harmon (1983) indicated that continental lizardite-chrysotile serpentinization probably occurred with waters of hydrothermal meteoric origin at relatively shallow levels in the Earth's crust. This is in contrast to antigorite that formed during regional metamorphism in the presence of metamorphic waters. The first examples of continental antigorites formed from ocean waters were reported by Burkhard and O'Neil (1988). The $\delta^{18}\text{O}$ values of lizardite-chrysotile serpentines range from +8.7 to -5.0 per mil and are often correlative with the $\delta^{18}\text{O}$ of the country rock. Pure antigorite has very restricted range of

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$\delta^{18}\text{O}$ (+4.7 to +8.7) (Wenner and Taylor 1974).

Wenner and Taylor (1971) devised an empirical serpentine-magnetite geothermometer based on estimates of the serpentine-water fractionation curve and analyses of natural magnetite bearing assemblages. Savin and Lee (1988) also estimated a serpentine-water fractionation curve based on empirical bond-type calculations. However both serpentine-water curves are similar above 300°C and the choice of curve for geothermometry can only affect the results at low temperatures. Oxygen isotope data indicate that lizardite-chrysotile serpentinization occurs at 85-185°C, whereas antigorites form at 220-460°C (Wenner and Taylor 1971).

Chrysotile asbestos veins of the cross-fiber type (fiber is oriented at a high angle to the vein wall) form at 200-300°C (Borshchevski et al. 1980, O'Hanley 1991). The $\delta^{18}\text{O}$ values of the chrysotile asbestos range from +2.8 to 13.5 and that of paragenetic magnetite from -4.4 to -6.8 per mil (Wenner and Taylor 1974, Magaritz and Taylor 1974, Ikin and Harmon 1983, Wicks and O'Hanley (1988). In this study we report the first results of oxygen isotope data on slip-fiber chrysotile asbestos veins (fiber oriented at a low angle to the vein wall), and also use the serpentine-magnetite geothermometer to define formation temperatures for slip-fiber chrysotile.

ANALYTICAL PROCEDURES

Serpentine minerals were identified using standard X-ray analytical techniques. The reflection peaks used for discriminating among antigorite, lizardite and chrysotile are those given by Wicks and O'Hanley (1988). All samples were examined for the 001 reflection of brucite.

Magnetite compositions were determined using a Jeol Super probe 733 at I.G.M.E. (Athens).

The samples were ground, washed with HCl to remove carbonate, and the magnetite was removed with a hand magnet. The magnetite concentrate was washed and reground. The process was repeated several times. Extraction of oxygen from serpentines and magnetites for isotopic analyses was accomplished by reacting powders with bromine pentafluoride for 18 hours at 600°C following the procedure of Clayton and Mayeda (1963). Before analyses magnetites were very finely ground to ensure complete extraction of oxygen. The oxygen released from the fluorination reaction was converted to CO₂ by reaction with a carbon rod at dull-red heat. Mass spectrometric analysis of the CO₂ was made using a VG Micromoss 602 ES machine. All oxygen isotope analyses are reported in per mil relative to SMOW scale. Accuracy is considered to less than ±0.25 per mil.

GEOLOGY AND MINERALOGY

The serpentinite body of Zidani is one of the several klippen that form the Livadi ophiolite complex (Nance 1981), located in northern Greece, near the Vourinos ophiolite complex (Fig. 1). The chrysotile asbestos deposit occurs in the northern part of the antigorite serpentinite body, which is thrust over the crystalline basement of the central Pelagonian Unit. Metaserpentinites consisting of metamorphic olivine + talc + ferritchromite occur in the eastern edge of the serpentinite body. Metaclastic schists and carbonates are thrust over the serpentinites (Fig. 1). Epidote-amphibolite dykes cross-cut the serpentinites and metaserpentinites in the area. The plagioclase of the amphibolites that are found in the serpentinites is albite whereas that of the dykes found in the metaserpentinites is of the peristerite series. Thus, the mineral assemblages indicate an increase in the metamorphic grade

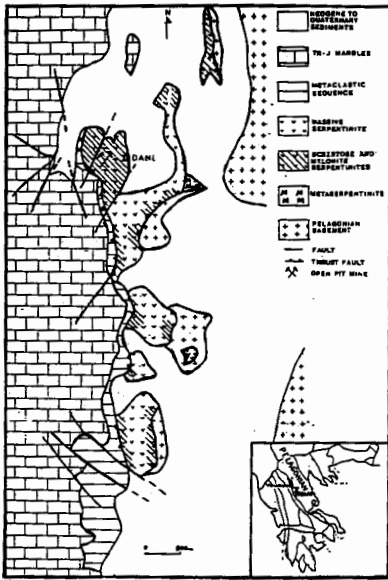


Fig.1: Geological map of the Zidani area (based on data of Mavrides and Kelepertzis (1982), and personal observations). The inset shows the location of the Zidani chrysotile asbestos deposit and its setting with respect to the Vourinos ophiolite complex and the Pelagonian Unit.

Magnetite forms strings parallel to the growth of the chrysotile fibers. Commonly picrolite is found along the asbestos vein walls. It consists of foliated antigorite and passes gradually or abruptly to silky chrysotile asbestos fibers.

The formation of the chrysotile asbestos is attributed to retrograde alteration of the antigorite serpentinite mainly during the brittle stage of deformation associated with thrust fault motion (Skarpelis and Dabitzias 1987, Karkanas 1994).

DESCRIPTION OF THE SAMPLES

Samples C18 and C29 are from the fish-like serpentinite bodies. They consist of interlocking to interpenetrating textures of antigorite. Cr-magnetite usually forms well-developed blebs. Some of them are rimmed by pure magnetite. Strings of pure magnetite are also present.

Samples C6 and C101 are from the picrolite material that parallels the chrysotile asbestos veins. They consist of fine, foliated antigorite crystals. Blebs and strings of magnetite develop mainly at the edges of the picrolite material.

Sample C171 consists of silky, flexible chrysotile fibers. C17 consists

towards the east (Karkanas 1994).

A dense anastomosing cleavage cross-cuts the asbestos-bearing serpentinites forming small fish-like serpentinite bodies. These fish-like bodies are cemented by slip-fiber chrysotile asbestos. The asbestos fibers formed concurrent to the development of the fish-like bodies (Skarpelis and Dabitzias 1987).

The serpentinite consists of antigorites exhibiting interlocking and interpenetrating textures, but relics of lizardite pseudomorphic textures are also rarely present. Brucite was not found. Chromite relict cores are found mainly in samples with the relict pseudomorphic textures. The chromites are usually rimmed by secondary Cr-magnetite. The development of the interlocking and interpenetrating antigorite textures is accompanied by the appearance of magnetite in well-developed blebs. These blebs have a Cr-magnetite composition (Table 1). Also, pure magnetite is present as small disseminated grains (anal. C18(2), Table 1). The stable spinel in antigorite serpentinites is Al-poor magnetite, Cr-magnetite, or ferritchromite, depending on the local Cr/Fe³⁺ ratio in the rock. However, ferritchromite is more typical of the metaserpentinites (Evan and Frost 1975). Relict chromite crystals are often absent from antigorite serpentinites (Wenner and Taylor 1971).

Chrysotile asbestos fibers replace antigorite "in situ" in shear planes or fill "shear veins" (after Durney and Ramsay 1973) at the edges of the fish-like serpentinite bodies.

Table 1: Representative microprobe analyses of magnetite from antigorite serpentinites at Zidani

	C6	C101	C29	C18(1)	C18(2)
SiO ₂	0,70	0,86	0,48	0,43	0,00
TiO ₂	0,00	0,00	0,00	0,00	0,25
Al ₂ O ₃	0,38	0,07	0,16	0,27	0,00
Fe ₂ O ₃ *	62,79	63,09	66,49	66,95	67,70
Cr ₂ O ₃	4,21	4,19	1,25	0,97	0,30
FeO	29,55	29,08	28,70	30,12	28,94
NiO	0,44	0,70	0,91	0,62	0,00
MnO	0,39	0,36	0,34	0,40	0,00
MgO	0,97	1,32	1,03	0,39	1,08
CoO	0,16	0,00	0,00	0,00	0,14
Total	99,59	99,67	99,36	100,15	98,41
Numbers of ions on the basis of 32(O)					
Si	0,21	0,26	0,15	0,13	0,00
Ti	0,00	0,00	0,00	0,00	0,06
Al	0,14	0,03	0,06	0,10	0,00
Fe ³⁺	14,42	14,44	15,34	15,41	15,81
Cr	1,02	1,01	0,31	0,23	0,07
Fe ²⁺	7,53	7,40	7,36	7,70	7,51
Ni	0,11	0,17	0,22	0,15	0,00
Mn	0,09	0,09	0,09	0,10	0,00
Mg	0,44	0,60	0,47	0,18	0,50
Co	0,04	0,00	0,00	0,00	0,05

* Fe₂O₃ estimated on the basis of 24 cations

fractionation curve of Becker and Clayton (1976). The values are quite high (8.3 to 9.8 per mil). This range is much higher than anticipated for meteoric-water based fluids, and must be presumed to be representative of metamorphic fluids. Igneous fluids are not considered probable because of the absence of magmatic activity in the study area.

Table 2: Temperatures of formation for serpentine-magnetite pairs and calculated $\delta^{18}\text{O}$ for waters

Sample	mineralogy	$\delta^{18}\text{O}$ (SMOW) serpentine	$\delta^{18}\text{O}$ (SMOW) magnetite	Δ (serp-magn)	T°C	$\delta^{18}\text{O}$ (SMOW) water
C171	C	7,7	2,8	4,9	450	9,8
C17	C	6,7	1,5	5,2	420	8,8
C18	A	6,8	1,8	4,9	450	8,8
C29	A	7,2	3,3	3,9	600	**
C6	P	6,2	1,4	4,8	460	8,3
C101	P	6,4	0,7	5,7	380	8,4

* Δ is the fractionation $\delta^{18}\text{O}$ (serpentine) - $\delta^{18}\text{O}$ (magnetite)

** not calculated (see text)

C=chrysotile asbestos, A=antigorite, P=picrolite (foliated antigorite)

of harsh, light yellow-green chrysotile fibers. Both samples of chrysotile have magnetite forming strings in between the chrysotile fibers.

ANALYTICAL RESULTS

$\delta^{18}\text{O}$ analyses and $\text{O}^{18}/\text{O}^{16}$ fractionations (Δ serpentine-magnetite) for coexisting serpentine and magnetite from the serpentinite samples examined in this study are given in Table 2. The $\delta^{18}\text{O}$ values of serpentine and magnetite have a very restricted range: $\delta^{18}\text{O}$ of magnetite varies from +0.7 to +2.8 and $\delta^{18}\text{O}$ of serpentine from 6.2 to +7.7 per mil. The temperatures were calculated using the serpentine-magnetite geothermometer of Wenner and Taylor (1971). The high temperature of sample C29 is because the magnetite was contaminated with serpentine and therefore gave a too high analysis. The results as a whole indicate temperatures of around 400-450°C, and are consistent with metamorphic conditions.

The $\delta^{18}\text{O}$ of water is calculated using the magnetite-water

DISCUSSION

Antigorite forms at higher temperatures than either lizardite or chrysotile (Wenner and Taylor 1971). The antigorite out-reaction during prograde metamorphism is antigorite = forsterite + talc + water and occurs at 500-600°C (P(H₂O) 1-10Kb) (Evans et al. 1977, Chernosky et al. 1988). The data obtained from antigorite-magnetite pairs of this study are comparable with previous oxygen isotope data on antigorite serpentinites and the stability of antigorite. The hemical inhomogeneity of the magnetite is not expected to cause any serious deviations in the serpentine-magnetite geothermometer.

Chrysotile is the low-temperature, low-pressure serpentine mineral (O'Hanley et al. 1989). In prograde metamorphism chrysotile reacts to antigorite at 260-300 °C (Evans et al. 1977, Chernosky et al. 1988). Chrysotile has been frequently observed to replace antigorite during retrograde metamorphism of serpentinites (Chidester et al. 1978, Skarpelis and Dabitzias 1987, O'Hanley 1991).

As has previously mentioned, oxygen isotope data have indicated that chrysotile asbestos forms at temperatures of 200-300°C. In contrast, in this study the $\delta^{18}\text{O}$ values of chrysotile asbestos indicate formation temperatures of 400-450°C. No changes in isotopic composition are evident during the alteration of antigorite to chrysotile. This consideration includes the picrolite which is probably a bridge-phase in the alteration process. It must be also pointed out that the $\delta^{18}\text{O}$ does not change significantly in either lizardite-chrysotile or antigorite serpentinites unless there is a chemical reaction as in the replacement of antigorite by chrysotile (Kyser 1987, Schandl et al. 1990). Consequently, the oxygen isotope values are unaffected by weathering alteration.

In addition, there is no evidence in the results for alteration processes involving hydrothermal meteoric waters. This is in contrast with previously published chrysotile asbestos isotopic data which indicated an hydrothermal meteoric origin of the asbestizing solutions (Borshchevsky et al. 1980, Magaritz and Taylor 1974, Ikin and Harmon 1983). In the Zidani asbestos deposit the alteration of the original antigorite assemblage was not accompanied by a change in isotopic composition, indicating that probably only small amounts of fluid were involved. This fluid could be a meteoric-water fluid, but only if it were present in such a small amounts that it could not change the $\delta^{18}\text{O}$ of the minerals. Given the absence of brucite, the appropriate reaction for the alteration of antigorite to chrysotile is that proposed by O'Hanley (1991): antigorite + 0.07H₂O = chrysotile + 0.11 SiO₂(aq). H₂O is stoichiometrically low so that this reaction is essentially a solid-solid one. However, serpentine recrystallization occurs in the presence of a fluid, although H₂O may not be consumed or produced during the process (O'Hanley 1991). In the case of Zidani, although H₂O might be a catalyst, it was not present in sufficient amounts to change the isotopic composition of the original serpentine assemblage.

The slip-fiber chrysotile asbestos of Zidani is the first reported example of chrysotile with a metamorphic water signature. In addition, this may indicate a different origin for the slip-fiber deposits from the so far studied cross-fiber types.

CONCLUSIONS

$\delta^{18}\text{O}$ data on the Zidani serpentinites indicate that isotopic compositions were not changed during the alteration of antigorite to chrysotile asbestos. Thus suggesting that probably only small amounts of fluid were involved.

The results as a whole indicate metamorphic temperatures of around 400-450°C, which are assigned to the conditions of the antigorite formation.

The calculated $\delta^{18}\text{O}$ of the waters are metamorphic values. There is no evidence that hydrothermal meteoric waters were involved during the serpentinization processes.

The results point to a different origin of the slip-fiber chrysotile asbestos deposits from the so far studied cross-fiber types.

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