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A WATER-BEARING ANDRADITE FROM THE TOTALP
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During the course of the investigation of the Totalp serpentine complex, belonging to a lower Austroalpine nappe, that lies at the base of the big Austroalpine overthrust, an unusual garnet was found (Peters, 1963). From the x -ray and optical data it was assumed to be a water-bearing andradite, but at that time there was not enough material to confirm this by other analytical methods.

These garnets are found in opicalcites, occurring alone or in little aggregates together with calcite, serpentine minerals (chrysotile and lizardite), and commonly with magnetite (Fig. 1).

SAMPLE PREPARATION

A 30 kg rock sample was crushed and ground to less than 100 microns. The garnets were enriched from the sieve fraction 40–63 μ with heavy liquids (methylene iodide and Clerici solution) and by magnetic separation. Finally the concentrate was purified by handpicking. Under the microscope and with x -ray analysis no impurities could be detected.

OPTICAL AND X-RAY DATA

Macroscopically the garnets are light green, in thin section almost colorless. The index of refraction measured in Na-light is 1.822 ± 0.003 (for pure andradite $n = 1.887$). X -ray diffraction patterns of these garnets are very similar to patterns obtained from pure andradite. However the cell edge $a = 12.08 \pm 0.005$ Å, calculated from the (400), (800), (840), (880), (12 20) and (12 22) reflections, is greater than the cell edge of pure andradite ($a = 12.05$ Å). In hydrogrossular substitution of H for Si causes an increase in cell edge and a decrease in refractive index as compared to pure grossular. This same substitution could also explain the optical and x -ray data of this garnet.

DTA

There was not enough material to make a DTA analysis with our normal set up, which requires 200 mg of sample. To get a DTA analysis however a $\frac{1}{2}$ mm diameter, 1 mm deep hole was bored in the head of a thermocouple and filled with the sample. Around the thermocouple was put fired Al_2O_3 ; this alumina was also used as reference material. In this way fairly good DTA-curves were obtained with 2–3 mg samples (Fig. 2).

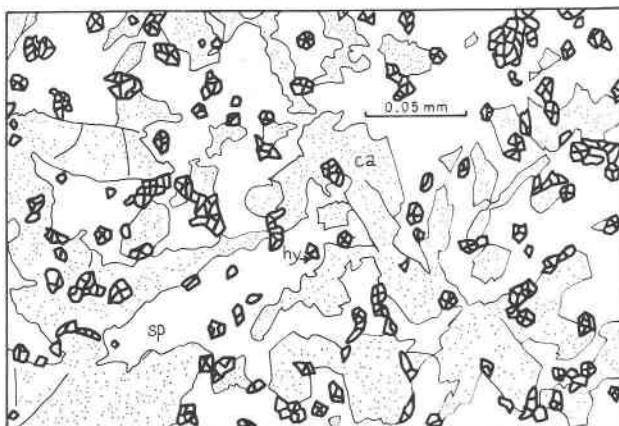


FIG. 1. Water-bearing andradite (hy) with calcite (ca) and serpentine minerals (sp) in ophticalcite. TP 180.

Up to 1000° C. no reactions were registered. Around 1190° C. a series of endothermic reactions occurred, produced by the decomposition and melting of the sample. The fired sample, heated a second time, only showed a single endothermic reaction, due to melting. The loss of H₂O

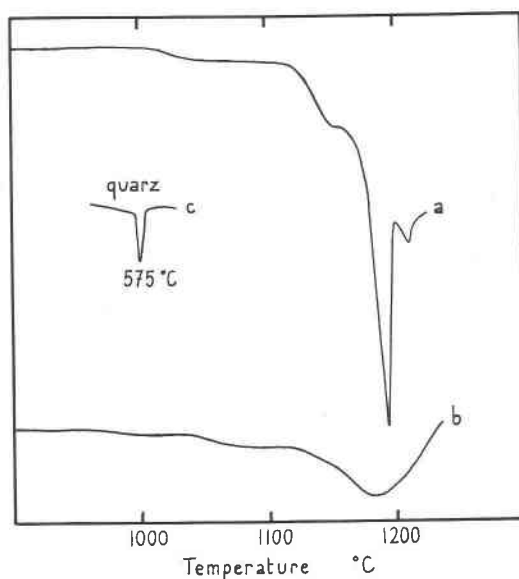


FIG. 2. DTA curves. a) Water-bearing andradite b) Fired water-bearing andradite c) The same amount of quartz for comparison. Heating rate 9.5° C./min.

obviously gave no detectable reaction, probably the result of the low H_2O content. Frankel (1959) gives a DTA curve for hydrogrossular which showed also only a decomposition reaction at 1100°C .

INFRARED SPECTROSCOPY

Infrared spectra in the 2500 to 4000 cm^{-1} region were obtained with a Perkin Elmer Model 13 using a CaF_2 prism. CsBr pellets and hexachlorobutadiene were used to dilute the samples. The garnet showed (Fig. 3) a broad OH-band at 3380 cm^{-1} due to absorbed H_2O and two other bands at 3525 cm^{-1} and 3660 cm^{-1} . These last two bands are caused by the OH vibrations resulting from the H for Si substitution in the garnet lattice.

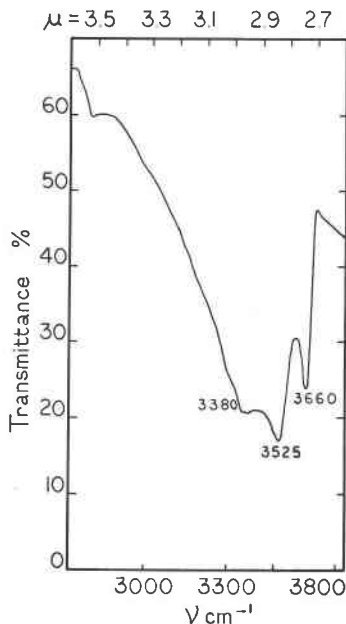


Fig. 3. Infrared spectrum of water-bearing andradite in the range 2500 – 4000 cm^{-1} .

For comparison the infrared spectrum of a hydrogrossular sample from South Africa (Frankel, 1959) showed a major absorption band at 3620 cm^{-1} and a minor band at 3660 cm^{-1} . Infrared spectra from normal andradite, occurring as fissure mineral in the Totalp serpentinite, show no absorption bands in this region.

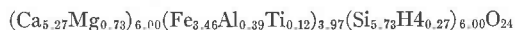
CHEMICAL ANALYSIS

A quantitative chemical analysis of the garnet by emission spectroscopy was kindly made by Dr. H. Schwander. The analytical procedure

TABLE 1. CHEMICAL ANALYSIS OF WATER-BEARING ANDRADITE FROM THE TOTAL SERPENTINE, DAVOS, SWITZERLAND

Weight %		Number of ions on the basis of 24 (0)	
SiO ₂	35.0	Si	5.73
Al ₂ O ₃	2.0	OH/4	0.27
Fe ₂ O ₃	28.0	Al	0.39
CaO	30.0	Fe	3.46
MgO	3.0	Ti	0.12
TiO ₂	1.0	Mg	0.73
Na ₂ O	trace	Ca	5.27
K ₂ O	trace		
MnO	trace		
H ₂ O	1.0		
Total	100.0		

followed is described by Wenk *et al.* (1963). The value for H₂O⁺ is approximate; it was obtained by comparison of the intensities of the OH absorption bands of the garnet with those from an analysed idocrase (Peters, 1961). The chemical analysis is shown in Table 1, and the formula derived from it is:



The anhydrous composition, expressed in the end members of the garnet group is: andradite 90%, pyrope 10%.

DISCUSSION

Hibschite or hydrogrossular, the water-bearing equivalent of grossular has long been known from contact-metamorphosed limestones (Cornu, 1905; Belyankin and Petrov, 1941), metasomatically altered anorthosites and pyroxenites (Frankel, 1959), and rodingites (Bilgrani and Howie, 1960). Yoder (1950) synthesized hydrogrossular solid solutions below 850° C. and 2 Kb; Roy and Roy (1957) give values for the maximum stability that are 300–400° C. lower than Yoder's data.

The similarity in the mode of occurrence and the complete solid solution between grossularite and andradite make it likely that a water-bearing equivalent for andradite should exist also. The cell edge of this garnet ($a_0 = 12.08$) is greater and the refractive index ($n = 1.822$) is lower than the calculated (using the data of Skinner, 1956) values for the anhydrous garnet andradite₉₀ pyrope₁₀: $a = 11.99 \text{ \AA}$ and $n = 1.870$. These facts, to-

gether with the OH vibration bands in the infrared spectra and the chemical data, show that such a water-bearing andradite exists.

This water-bearing garnet occurs in opicalcites accompanying a partly serpentinized alpine-type peridotite. Field and laboratory data (Peters, 1963) indicate that these opicalcites were formed when the crystalline, but not completely cool, peridotite was transported into soft, water-bearing, carbonate-rich sediments. Later Alpine metamorphism was of a low grade; these rocks are in the "Stilpnomelanzone" of Niggli (1960). Our findings suggest that the water-bearing andradite crystallized during formation of the opicalcites; whether formed then or during the metamorphism, the formation must have taken place at relatively low temperatures and pressures in the presence of water.

ACKNOWLEDGMENTS

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