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A SPECTRAL EXAMINATION OF SERANDITE  
FROM STE. HILAIRE, QUEBEC

by

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MINERAL SCIENCES DIVISION

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INTRODUCTION

At the request of Drs. G. Perrault and W.E. Trzcienski of the Department of Mineralogical Engineering, École Polytechnique, Montreal, the author agreed to undertake a spectral examination of specimens of partly altered serandite from Mont Ste. Hilaire, Quebec. This request arose because of the need to understand the processes that led to the formation of the final alteration product, a black Mn oxide having the pseudomorphology of serandite.

Accordingly, the author received a hand specimen containing a large mass of the Mn oxide, and a partly altered crystal of serandite, zones of which, in thin section, varied from the clear pink of unaltered serandite, to clear yellow-brown and to black. Although several other specimens were also received, only the two described above were examined spectrally. This report describes the nature and the results of the investigation.

EXPERIMENTAL

Measurement of Spectra

Pink and yellow-brown zones of "serandite" crystal

A microscope-spectrophotometer combination (Faye and Nickel, 1970) was used to measure the unpolarized absorption spectra of a clear pink zone and a yellow-brown zone (A and B respectively in Fig. 1) of the partly-altered serandite crystal. Prior to the spectral measurements, the polished (001) face of

the crystal was mounted on a microscope slide, and, using lapidary techniques, the specimen was thinned to a 0.04 cm thick plate.

#### Black Mn oxide phase

Fragments were broken from the large mass of the black Mn oxide phase. These were crushed and ground in a mortar and the resulting powder was mullied with a low-viscosity mineral oil. Because even the thinnest film of mull did not transmit light, the measurement of the absorption spectrum by the microscope technique of Faye (1971) was not possible.

#### Microprobe analysis of "serandite" crystal and fragment of Mn oxide

Microprobe analysis (by D.R. Owens) confirmed that the black alteration product in the "serandite" crystal is essentially a Mn oxide containing ~0.4% Fe, a substantial concentration of calcium, and very little silica. The Fe concentration of the unaltered serandite was found to be ~0.2%.

An analysis of a polished section of a fragment of the massive Mn oxide gave Mn ~53%, Co ~5%, K ~0.8%, and Si ~0.3%.

### DISCUSSION OF SPECTRA

#### Pink zone

Spectrum A in Fig. 1 is that of a clear pink zone of the partly altered crystal. As expected, it is typical of unaltered serandite (Manning, 1968). That there is only weak absorption in 900 to 1200 nm region is consistent with the low  $\text{Fe}^{2+}$  concentration (~0.2%) (e.g. Burns, 1970; Faye, 1972).

#### Yellow-brown zone

In spectrum B, the d-d bands of  $\text{Mn}^{2+}$ , between approximately 400 and 500 nm, are largely "swamped" by the intense absorption edge of a band that is located in the ultraviolet region. It is known that absorbance due to  $\text{O}^{2-} \rightarrow \text{Fe}^{3+} \text{ Fe}^{3+}$  is centered at

~200-250 nm in ferromagnesian silicates (Faye et al, 1974), glasses and aqueous solutions (Steele and Douglas, 1965) and that its low-energy wing is often responsible for the yellow to brown colour of specimens containing low to moderate concentrations of  $\text{Fe}^{3+}$ . Because charge transfer from oxygen to either  $\text{Mn}^{2+}$  or  $\text{Fe}^{2+}$ , in relatively high concentration, does not produce appreciable absorption in the visible region, it is probable that the uv absorption edge is indeed due to  $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$  charge transfer.

Because the sharply-defined yellow-brown zones of the crystal plate did not extend through its complete thickness, it was not possible to estimate the proportion of the iron in the oxidized state.

The spectra in Fig. 1 indicate that in the yellow-brown zones a substantial fraction of the iron (which microprobe analysis showed to be fairly uniformly distributed throughout the unaltered serandite) is in the ferric state, and that the manganese is present as  $\text{Mn}^{2+}$ . This is consistent with the preferential oxidation of  $\text{Fe}^{2+}$  over that of  $\text{Mn}^{2+}$  according to the respective oxidation potentials of -0.7 and -1.5V for these ions.

#### Black Mn oxide phase

As indicated above the absorption spectrum of the Mn oxide phase could not be measured because of its opacity. Microprobe analysis showed the iron content of this phase to be ~0.4%; even if this were all  $\text{Fe}^{3+}$  the intensity of the  $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$  charge-transfer absorption would be insufficient to produce a black colour. It seems, therefore, that the intense absorption in the visible region is associated with manganese in higher oxidation states, e.g.  $\text{Mn}^{3+}$  and/or  $\text{Mn}^{4+}$ . This is also consistent with the relatively high concentration of manganese (~53%) in the oxide.

$\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  are  $d^4$  and  $d^5$  ions respectively and both exhibit spin-allowed crystal field bands in the visible region. It is unlikely, however, that these bands alone would be

sufficiently intense to produce a black colour in a very thin section or mull. Therefore, it is proposed that  $O^{2-} \rightarrow (Mn^{3+}, Mn^{4+})$  charge transfer is of appreciable intensity in the black Mn oxide and that the low-energy wing of the absorption envelope (analogous to the  $O^{2-} \rightarrow Fe^{3+}$  feature in spectrum B of Fig. 1) may well be the principal absorber even in the visible region (Manning, 1973).

Depending upon structural considerations metal-metal charge transfer such as  $Mn^{2+} \rightarrow Mn^{4+}$  could also conceivably cause strong absorption in a mixed oxide.

#### SUMMARY

The clear pink zones of the "serandite" crystal are coloured by the crystal-field bands of  $Mn^{2+}$  alone; the yellow-brown zones are coloured by a combination of these bands and absorption due to  $O^{2-} \rightarrow Fe^{3+}$  charge transfer. The Mn oxide phase in the "serandite" is considered to be black because of intense absorption due to  $(O^{2-} \rightarrow Mn^{3+}, Mn^{4+})$  charge-transfer, and possibly to  $Mn^{2+} \rightarrow Mn^{4+}$  charge transfer as well.

#### ACKNOWLEDGEMENTS

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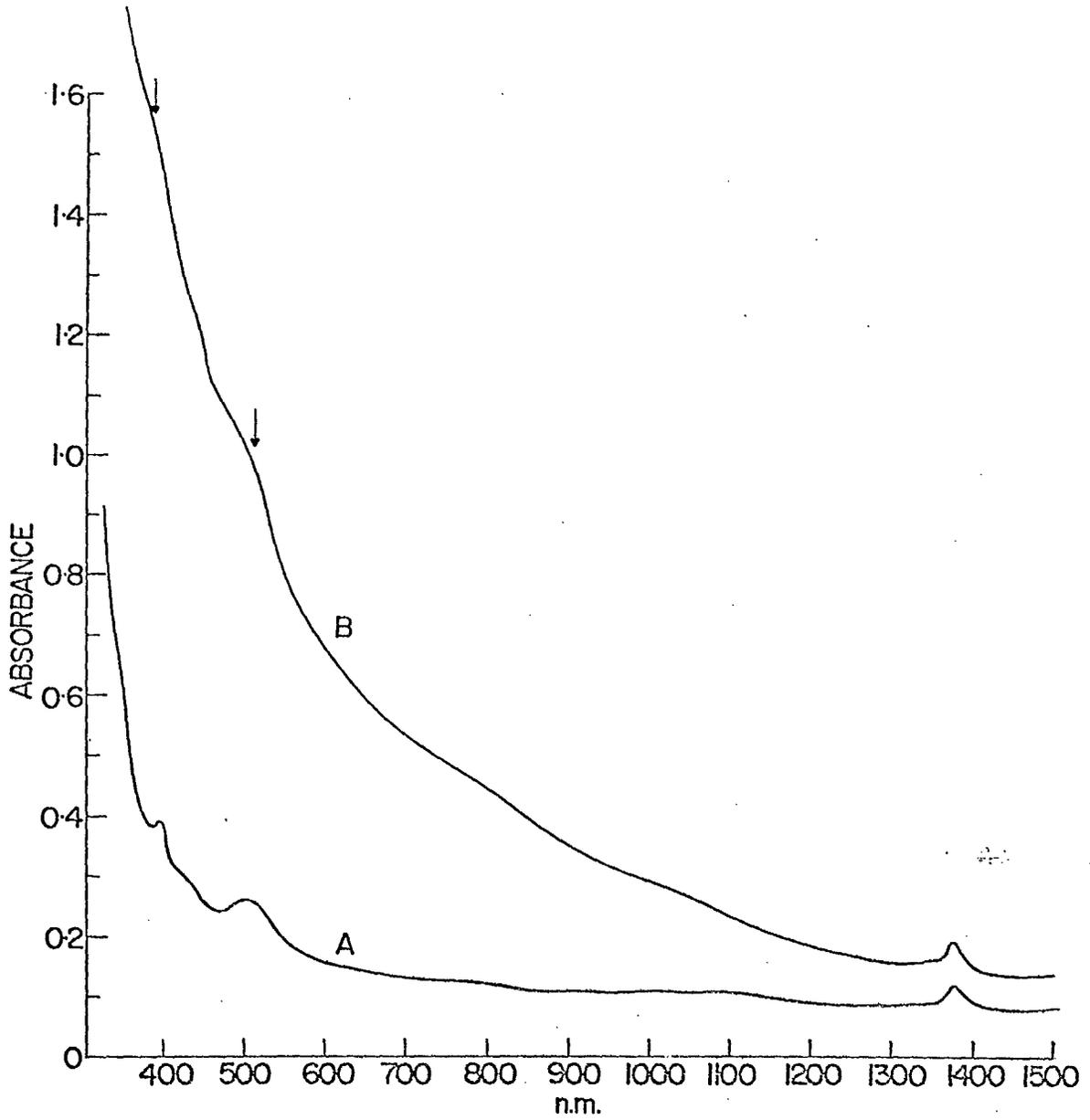


Fig. 1. - A and B are respectively unpolarized spectra of a pink zone and a yellow-brown zone of partly altered serandite crystal.