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Strontium in huntites from Geelong and Deer Park, Victoria, Australia

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Abstract

Huntite containing 1.86% SrO has been found in weathered basalt from Geelong, Victoria. X-ray diffraction (XRD) and infrared spectroscopy (IR) and scanning electron microscopy indicated that the Sr was not present in a separate phase but was substituted for Ca in the huntite structure. Another huntite from Deer Park, Victoria, also contained similar amounts of SrO. Weight loss and differential thermal curves are presented for the Geelong huntite. Energy dispersive X-ray analysis identified Sr in aragonite from Geelong. This was determined at 1.89% SrO by chemical methods and might have been the source of the Sr in the huntite.

Introduction

After huntite, $Mg_3Ca(CO_3)_4$, was recognized by Faust (1953) as a new mineral, it has been found in many other localities and in association with some other carbonate minerals. In Australia, huntite has been reported from Tea Tree Gully, South Australia, as a weathering product of dolomitic rock (Skinner 1958); from Katherine, Northern Territory, as localized nodules in a soil layer overlying weathered basalt (Veen and Arndt 1973); and from Deer Park, Victoria, as filling vesicles of the weathered basalt, in the form of nodules in the indurated fossil soil, and as small nodules in narrow clay seams of the newer basalts (Cole and Lancucki 1975).

Recently, Shayan and Sandy (1983) found huntite in large vesicles (already lined with a mixture of dolomite and magnesite) of altered basalt at Geelong, Victoria (Fig. 1). This huntite contained 1.86% SrO, but the nature of the strontium in huntite was not determined. Faust (1953) mentioned that his specimen no. N.M.186 contained, among a number of other elements of similar concentration, a few hundredths of one per cent, or less, of Sr. Except for a huntite containing 0.43% SrO (reported from China by Baogui and Yueming (1975)), no other reference has been found to huntites containing appreciable amounts of strontium. Although Cole and Lancucki (1975) did not report Sr in their huntite, preliminary examination of another sample of huntite from Deer Park indicated that it contained an amount of Sr similar to that in the Geelong huntite. The nature of Sr in these two huntites is examined in this paper.

Experimental

Portions (0.1 g) of the huntite samples were dissolved in 1 N HCl and then diluted for analysis for Ca, Mg, Sr, Fe and Mn, using atomic absorption spectrophotometry. Determination of CO_2 was carried out by the Australian Mineral Development Laboratories (AMDEL). XRD powder patterns were obtained (½° of 2θ per minute) using a diffractometer and Cu$K\alpha$ radiation. IR spectra were run on a Beckman IR20 or a Perkin-Elmer 1430 infrared spectrometer using from 0.5 to 10 mg of sample and 200 mg KBr as disks pressed cold under vacuum. A Stanton Redcroft model ST 781 thermal analyser was used for combined differential thermal analysis (DTA) and thermogravimetry (TG). A scanning electron microscope equipped with an EDAX (energy dispersive analysis of X-rays) unit was used to obtain the qualitative composition of the samples.

Results and discussion

Results of chemical analysis of the huntite from Geelong are given in Table 1 together with those taken from Cole and Lancucki (1975) for Deer Park huntite. Although the chemical analysis of the latter does not include SrO, EDAX and chemical analysis of another sample of Deer Park huntite shows that Sr is present in both huntites (Fig. 2 and Table 1). The Sr in the huntites could be present either as a separate phase carbonate, i.e., strontianite ($SrCO_3$), or in the structure of huntite, substituting for Ca. Although pure samples of huntite had X-ray powder diffraction patterns similar to the published patterns of huntite (e.g., ASTM card 14-409), one sample with small feldspar impurity showed weak XRD lines at 3.54 and 3.47Å which correspond to the strongest two lines of strontianite. When 3% strontianite was added to pure huntite these lines also appeared. Therefore, attempts were made to investigate the presence of strontianite with huntite using infrared spectroscopy, DTA, scanning electron microscopy and EDAX.

Figure 3 shows the IR spectrum of the Geelong huntite (0.5 mg sample) in the region 250–2000 cm^{-1}, which was very similar to that of Deer Park huntite. Resolving these

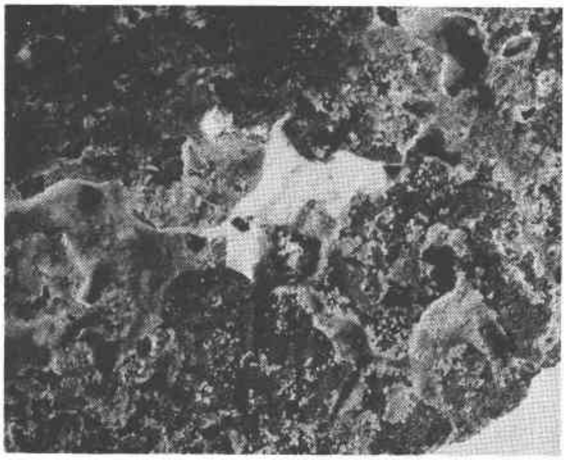

Fig. 1 White huntite occurring in vesicles of altered basalt from Geelong. The vesicles are lined with a mixture of dolomite and magnesite. Magnification 2.2×.

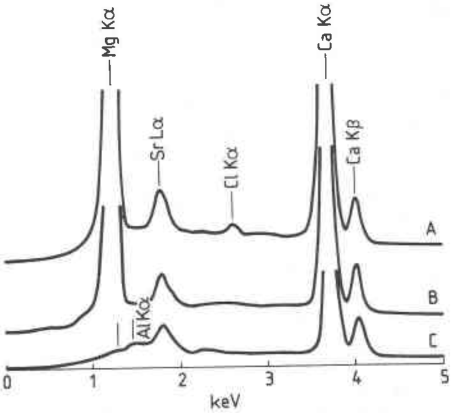

Fig. 2 Energy dispersive X-ray spectra of (A) huntite from Deer Park, (B) huntite from Geelong, and (C) aragonite from Geelong, all showing the presence of Sr, as shown by the strontium Lα line. Vertical scale is the number of X-ray counts, which depends on the length of analysis time and is not the same for the three samples.

two minerals in the IR spectrum is rather difficult since their absorption bands are close to each other. If the huntites contain strontianite, then because of its very small amounts the weak absorption band at 1073 and the doublet at 699 and 706 cm^{-1} which do not overlap those of huntite, are not observed. The IR spectra of the huntites run on KBr disks containing as much as 10 mg sample did not show the 1073 cm^{-1} band, and only one absorption band at 700 cm^{-1} appeared rather than a doublet. Samples of the pure huntite with 3% added strontianite (10 mg in KBr disk) showed a very very weak band at 1073 cm^{-1}, and only one band at 702 cm^{-1}. Unfortunately, these bands are very weak in the strontianite spectrum and do not show up clearly at low concentrations. The published IR spectra of huntite (Adler and Kerr, 1963a; Van der Marel and Beutelspacker 1976, p. 246; Scheetz and White, 1977) show two pairs of strong IR absorption bands in the spectrum, one at 860 to 890 cm^{-1} and the other at 1435 to 1545 cm^{-1}; the two absorption bands of each pair have similar intensities. In the IR spectra of huntites from Geelong and Deer Park, however, the intensities of the bands at 860 and 1435 cm^{-1} have been enhanced relative to those at 880 and 1505 cm^{-1} respectively, and a band at 1455 cm^{-1} is also observed. The strongest two absorption bands of stron-

Table 1. Chemical analysis of huntite samples from Geelong and Deer Park

	Geelong (%)	Deer Park * (%)
MgO	33.27 (32.50)	33.0 (33.66)
CaO	13.24 (13.61)	15.0 (14.00)
SrO	1.86 (1.54)	n.d. (1.82)
MnO	0.030	0.01
FeO**	0.026	n.d.
Fe_2O_3	n.d.	0.11
CO_2#	48.18	47.8 (48.84)
SO_3	n.d.	<0.01
P_2O_5	n.d.	0.015
SiO_2	n.d.	0.20
Cl	n.d.	0.90 (1.33)
H_2O^-	0.67	1.00
H_2O^+	n.d.	1.30 (1.50)
insoluble	1.90	n.d.
Total	99.26	99.25
	Molar ratios	
MgO	3.48 (3.32)	3.06 (3.34)
CaO	1.00 (1.00)	1.00 (1.00)

* taken from Cole and Lancucki (1975)
** total Fe shown as FeO
\# determined by AMDEL for Geelong huntite
n.d. = not determined.

Note: Figures in brackets for Geelong huntite are checks made by AMDEL on the same sample as that analysed by the author. Those for Deer Park huntite are an analysis by AMDEL (Report No. 2651/83) of the actual Deer Park sample used in this work.

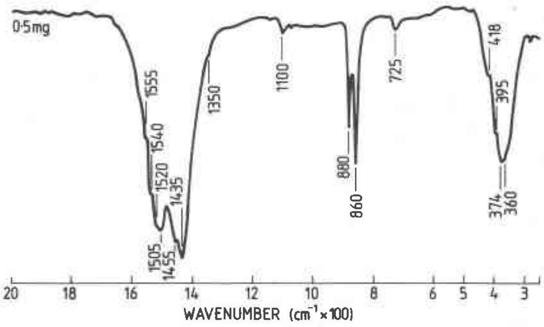

Fig. 3 Infrared spectrum of Geelong huntite, which was very similar to that of the Deer Park huntite.

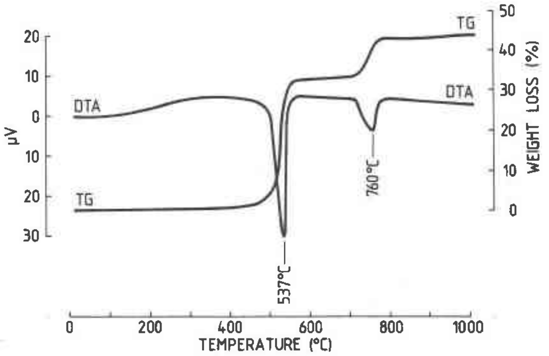

Fig. 4 Combined DTA and TG curves for the Geelong huntite. Endothermic peaks at 537 and 760°C represent the decomposition of $MgCO_3$ and $CaCO_3$ components of huntite, respectively.

tianite occur at around 860 and 1450 cm^{-1} (Adler and Kerr, 1963b), and could possibly have enhanced those of the huntites. However, strontianite could not positively be confirmed from the IR evidence.

Combined DTA and TG curves of the Geelong huntite are shown in Figure 4, where the TG curve shows a 44% loss on heating to 1000°C, and the DTA curve shows two characteristic endothermic peaks at 537 and 760°C due to decomposition of the $MgCO_3$ and $CaCO_3$ components of huntite respectively. Strontianite would decompose above 1000°C, so its breakdown would not be observed. The temperatures of the two endotherms for the Geelong huntite are lower than those (570 and 850°C) reported by Faust (1953) and Cole and Lancucki (1975). However, there is evidence in the literature that the decomposition temperature can be influenced by the presence of impurity, the amount and particle size of the material used, and other experimental variables. When the Deer Park huntite was run under similar conditions to the Geelong material, decomposition temperatures of 539 and 767°C and a total weight loss of 49.5% were obtained. The latter value is less than that (58%) given in Figure 3 of Cole and Lancucki (1975). Inspection of these authors' original DTA and TG traces revealed that the weight loss scale in their Figure 3 is incorrect and the true weight loss is 45% (Cole and Lancucki, 1982). The smaller weight loss (44%) for the Geelong huntite is consistent with the presence of impurities that do not decompose at 1000°C (e.g., feldspar and possibly strontianite).

As suggested by Dr. George Rossman, individual grains of the huntite powder were examined under the SEM at high magnifications (10k), using EDAX. Among 100 grains examined, 98 showed the typical composition of huntite as seen in Figure 2B, and two grains contained much more Ca than Mg with no Sr, attributable to magnesian calcite. No grains were observed to contain Sr as the major component, indicating that Sr most probably existed in the structure of the huntite.

Faust (1953) suggested that huntite was formed during the late meteoric stage and was the last mineral to fill the cavities in the host rock. It is possible that strontium was derived from aragonite that had formed in an earlier stage. This mineral is abundant in a black altered basalt at Geelong and contains Sr, as Figure 2C shows. Chemical analysis of some aragonite crystals showed that the Sr content of aragonite amounted to 1.89% SrO. Holz and Holland (1965) have indicated that Sr-rich aragonite could be the source of Sr in strontianite. It is, therefore, likely that the solution rich in Mg and Ca, from which huntite precipitates, acted on aragonite to release Sr and this was coprecipitated with Ca and Mg during the formation of huntite.

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