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Structure model for kassite, $CaTi_2O_4(OH)_2$

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ABSTRACT

We have found the rare mineral kassite, $CaTi_2O_4(OH)_2$, in an unusual rock from Josephine Creek, Oregon. Using electron-diffraction techniques, kassite was observed to have a *b*-centered orthorhombic unit cell with dimensions $a = 0.908$, $b = 0.478$, and $c = 0.523$ nm. This cell is closely related to that given in the original description of kassite (Kukharenko et al., 1965) rather than the cell given in a more recent article by Evans et al. (1986). A crystal structure for kassite based on that of $CaSb_2O_6$ is proposed.

INTRODUCTION

Kassite is a rare mineral that contains common elements in simple proportions. In spite of this chemical simplicity, the literature describing kassite is confused. Kassite was first reported by Kukharenko et al. (1965), who found it in specimens from the Afrikanda massif on the Kola peninsula in the USSR, where it occurs in mariolitic cavities of alkalic pegmatites. They assigned kassite a chemical formula of $CaTi_2O_4(OH)_2$ and an orthorhombic unit cell with dimensions $a = 0.901(3)$, $b = 0.957(3)$, and $c = 0.527(1)$ nm. A second occurrence of kassite was reported from an iron deposit in Henan Province, China (Yu et al., 1982). Most of the properties attributed to kassite by Yu et al. agree with those of Kukharenko et al. (1965); however, the Chinese workers described kassite as optically uniaxial and suggested that the unit cell should be tetragonal.

Subsequently, Evans et al. (1986) reported kassite from the Diamond Jo quarry, which is in a nepheline syenite pegmatite at the edge of the Magnet Cove complex. Their study showed that although the sample from the Diamond Jo quarry has a chemical formula that agrees with kassite as reported by Kukharenko et al. (1965), in most other respects it is indistinguishable from cafetite ($CaFe_2Ti_4O_{12} \cdot 4H_2O$), a mineral that also occurs in the Afrikanda massif (Kukharenko et al., 1959). Based on their extensive crystallographic, petrographic, and gravimetric evidence, Evans et al. concluded that samples of kassite and cafetite from the Afrikanda massif had been intermixed by the Russian workers during their X-ray analysis. As a consequence of the work of Evans et al., the cafetite and kassite entries have been interchanged in Set 39 of the Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction file (ICDD, 1989).

We found several grains of kassite while doing a transmission electron microscopy (TEM) study of rutile in a specimen from Josephine Creek, Oregon. The Josephine Creek specimen contains an extraordinary assemblage of unusual minerals, including a large collection of oxides and alloys, some of which contain noble and rare-earth metals. Our attention was drawn to the kassite grains because they gave energy-dispersive X-ray (EDX) spectra with a Ca/Ti peak-height ratio of 1:2 rather than the 1:1 ratio exhibited by the perovskite that is abundant in the sample. Burton (1982), following an extensive petrographic study of the Josephine Creek specimen, concluded that it originated in the Earth's mantle.

The chemical formula determined from EDX spectra and electron microprobe analysis for the kassite from Josephine Creek is essentially $CaTi_2O_4(OH)_2$ (with Fe present below 2 at.%). Except for a halving of the *b* axis, the unit-cell dimensions as determined by TEM are as reported for kassite by Kukharenko et al. (1965). The latter result is contrary to that of Evans et al. (1986).

In this paper we describe the results of a TEM investigation of kassite from Josephine Creek and, by studying a synthetic analogue of kassite, propose a structure for the mineral. This structure is similar to that of lucasite (Nickel et al., 1987).

EXPERIMENTAL

The major minerals in our piece of the Josephine Creek specimen are rutile, ilmenite, perovskite, and sphene. The total specimen available to us was a spheroid approximately 1 cm in diameter, and so we were severely limited in the amount of material available for study. It was not possible to isolate the kassite from the specimen because of the small amount of kassite and because it is in intimate contact with the other minerals. Hence, suitable samples for TEM were prepared by crushing a small part of the specimen and dispersing the resulting grains over holey-carbon support grids. All TEM was done using a Philips 400T electron microscope fitted with a Tracor Northern EDX spectrometer and a Gatan electron energy-loss spectrometer. Individual minerals were identified in situ using the EDX spectrometer. Approximately ten μm-sized grains of kassite were identified and studied.

X-ray diffraction (XRD) study of the synthetic sample

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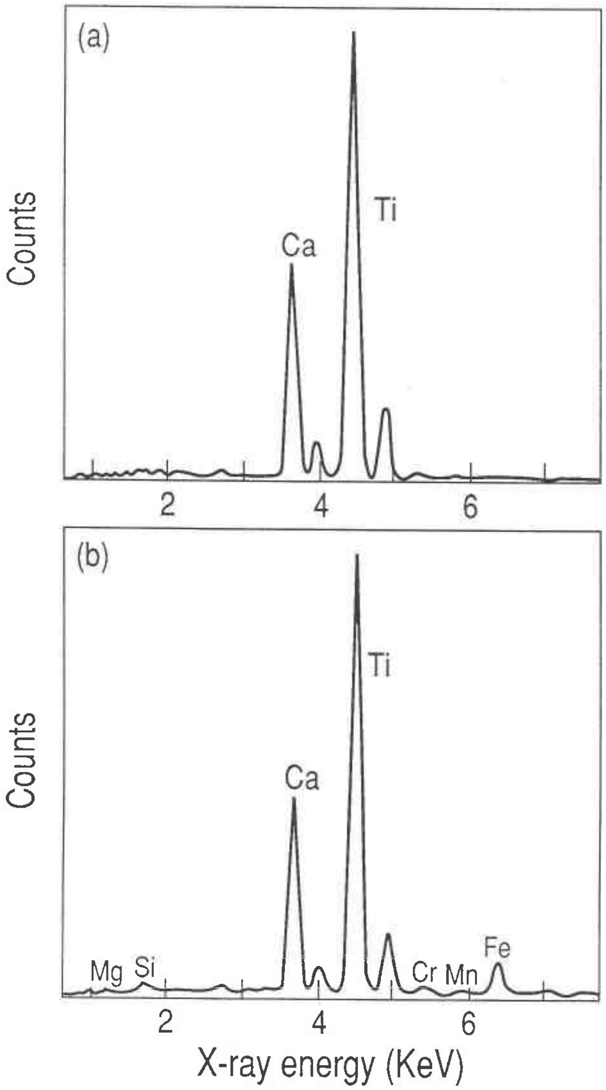

Fig. 1. EDX spectra of kassite from Josephine Creek, Oregon. (a) Spectrum from a typical kassite grain. (b) Spectrum from the grain containing the highest quantities of trace elements.

was done using a Philips PW1800 diffractometer and pressed powders. A Cambridge Instruments S250 scanning electron microscope fitted with a Link EDX system was used for imaging and chemical analysis of the synthetic specimen. Differential thermal analysis (DTA) of the synthetic sample was done on a Rigaku Thermoflex 8100 series instrument.

CHEMICAL COMPOSITION

Figure 1a shows a typical EDX spectrum of kassite from the Josephine Creek sample. Ca and Ti occur in major amounts, together with <1 wt% Cr and Mn. Quantitative analyses of kassite were obtained by using the other minerals in the specimen as standards to calibrate the detection efficiency of the EDX spectrometer for the elements of interest. Using perovskite as a standard, the atomic Ti/Ca ratio was determined to be 2.05 ± 0.07. This result is an average over analyses from several different grains of kassite, and the uncertainty represents the spread in the individual results.

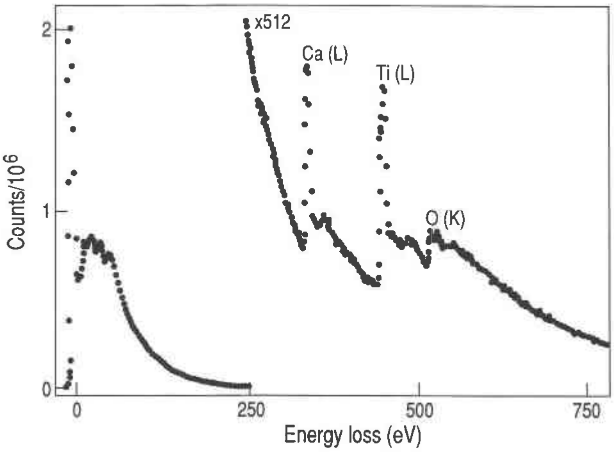

Fig. 2. EELS spectrum of kassite from Josephine Creek.

The concentrations of the minor elements vary from grain to grain. In some grains Fe occurs as a minor component, while it is present below the detection limit in others. Figure 1b is an EDX spectrum from the grain containing the largest amounts of the minor elements. The Fe/Ti atomic ratio from this spectrum is approximately 0.07, which is much less than the 0.50 Fe/Ti ratio expected for cafetite.

Electron energy-loss spectrometry (EELS) was used to determine the light-element concentrations in kassite from Josephine Creek. A kassite EELS spectrum is shown in Figure 2. It contains large peaks corresponding to Ca, Ti, and O energy losses. Quantitative EELS analyses using perovskite and sphene as standards confirmed the value of the Ti/Ca atomic ratio as determined by EDX analysis.

By examining EELS spectra in the energy range 0–1 keV it was possible to determine that O is the only element with an atomic number in the range 3–10 that occurs in kassite in significant proportions. Determining the concentration of O proved problematic because the extended structure of the Ti(L) energy-loss peak makes it difficult to obtain reliable background subtractions at regions in the spectrum around the O energy-loss peak. This difficulty leads to a large uncertainty in the value obtained for the O concentration. Using perovskite, sphene, and rutile as standards, the atomic O/Ca ratio was determined to be 5.7 ± 0.6.

During his study of the Josephine Creek specimen, Burton (1982) obtained electron microprobe analyses of kassite but was unable to identify it. Our EDX and EELS results are consistent with his electron microprobe analyses. The same compositions and totals were obtained by Dawson and Smith (1977, specimen 5, Table 4) from an unidentified kimberlitic Ca-Ti mineral. The microprobe results of both Burton and Dawson and Smith have low totals (≈90%). From the above experimental results we conclude that the chemical formula of kassite from Josephine Creek is essentially $CaTi_2O_4(OH)_2$. For the grain that had the highest concentrations of minor elements (Fig. 1b) the chemical formula is $Ca(Ti_{1.87}Fe_{0.13})_4O_{3.87}(OH)_{2.13}$.

CRYSTALLOGRAPHY

Selected-area electron diffraction (SAED) was used to determine that kassite from Josephine Creek has a *b*-centered orthorhombic cell with dimensions $a = 0.908$, $b = 0.478$, and $c = 0.523$ nm. By using Au evaporated onto the TEM grid for an internal standard, and by calibrating the diffraction camera length as a function of in-focus objective lens current (i.e., specimen height), the cell dimensions could be determined with an accuracy of ±0.3%. The unit-cell dimensions measured using SAED agree with those published by Kukharenko et al. (1965), except that the *b* axis is halved in our measurements (0.478 nm as opposed to 0.956 nm). The SAED patterns were examined for reflections that would indicate a doubling of the *b* axis, but no such reflections were found.

The *b*-centering and halved *b*-axis length of the cell determined by using SAED requires a different set of indices from those normally used for the XRD pattern of kassite. [See, for example, JCPDS powder diffraction file entry 20-243 (ICDD, 1989).] However, all lines that are indexed for the lattice proposed by Kukharenko et al. (1965) can also be indexed by using the cell with $b = 0.478$ nm.

The *b* centering of the orthorhombic cell means that the unit cell can also be described by a primitive monoclinic cell with dimensions $a = 0.524$, $b = 0.478$, $c = 0.523$ nm and $\beta = 119.9°$. The volume of this cell is such that there can be only one formula unit per unit cell. The lengths of the *a* and *c* axes of the monoclinic cell are nearly equal and the angle between them is nearly 120°; hence the cell is very close to hexagonal in dimensions. Convergent-beam electron diffraction from the [010] zone of the monoclinic kassite cell showed the pattern to be not only geometrically nearly hexagonal in dimensions but also that groups of reflections that would be equivalent in a truly hexagonal crystal [e.g., (100), (001), and $(10\bar{1})$, referenced to the monoclinic cell] have intensities that are similar for all crystal thicknesses. This similarity of the intensities and the length of the *b* axis suggests that the structure of kassite could be based on a hexagonal close packing of O atoms. In addition, it is reasonable to expect that in such a hexagonal net the Ti atoms would lie in octahedral sites.

One such structure is that of $CaSb_2O_6$ (Magneli, 1941; Wyckoff, 1965). The corresponding structure for $CaTi_2O_4(OH)_2$ is shown in Figure 3. The cations of the two different atomic species lie on alternate basal planes. We propose that kassite has a slightly distorted $CaSb_2O_6$ structure, which is also similar to that of lucasite, $CeTi_2(O,OH)_6$ (Nickel et al., 1987). It is interesting that in lucasite, because of a displacement of the Ce atoms, the repeat distance in the direction perpendicular to the close-packed O layers is doubled relative to that of the $CaSb_2O_6$ structure. If this doubling were applied to the cell dimensions for kassite given above (i.e., double the *b* axis), then the cell dimensions would be the same as those given by Kukharenko et al. (1965).

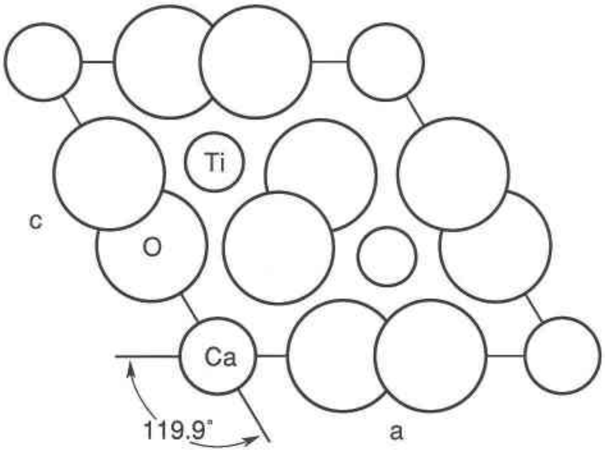

Fig. 3. Proposed structure for kassite. The structure is based on that of $CaSb_2O_6$.

SYNTHETIC ANALOGUE

A synthetic analogue of kassite has been described by Rudashevskii et al. (1977). This analogue is a by-product of the Bayer process in Al smelting and, in order to investigate the structure of kassite in more detail, we obtained a quantity of this by-product (known as flash-tank scale). The scale was found to be a three-phase mixture of kassite, cancrinite, and hematite. Rudashevskii et al. reported that synthetic kassite formed at temperatures in the range 100–250 °C, with pressures ranging from 30 to 70 atm. However, C. Cardille (Alcoa Australia Ltd.; personal communication) pointed out that kassite does not form below 180 °C, and that below this temperature the cancrinite in the scale is replaced by the related feldspathoid, noselite.

The sample was treated chemically to isolate the kassite from the other minerals in the scale. The cancrinite was dissolved by leaving approximately 10 g of powdered scale overnight in a solution of 50 mL of concentrated HCl and 250 mL of H_2O. The solution was then brought back to neutral pH by repeatedly centrifuging, decanting the supernatant, and adding H_2O. The treated powder was recovered by drying in an oven at 105 °C. Hematite was removed by leaving the acid-treated powder overnight in a solution of 7.5 g of sodium dithionite and 100 mL of H_2O at 60 °C. The treated powder was again recovered by repeated centrifugation, decantation, addition of H_2O, and finally oven drying.

An XRD trace of the acid-washed and dithionite-treated scale is shown in Figure 4a. The positions and intensities of the peaks in this pattern agree with those of Rudashevskii et al. (1977). The unit-cell dimensions for the

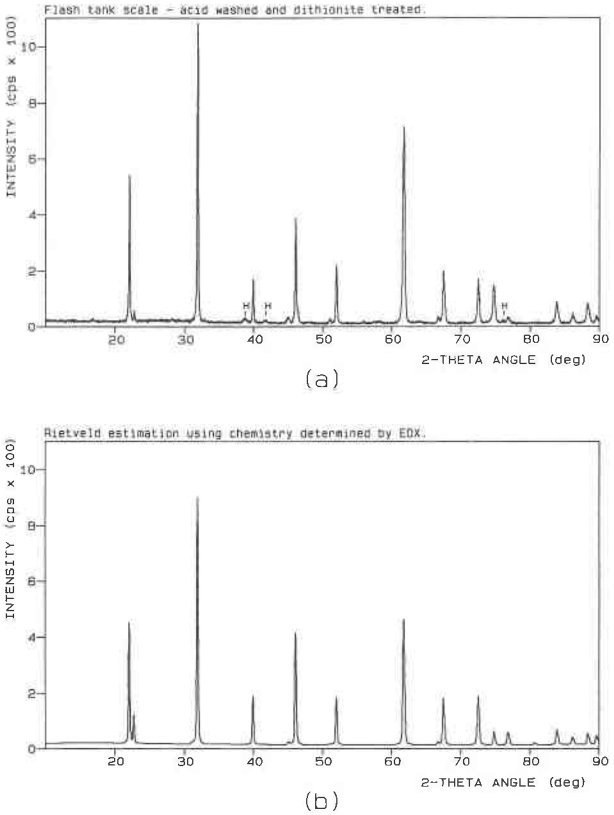

Fig. 4. **(a)** Experimental XRD pattern for synthetic kassite. (Peaks resulting from hematite are marked H.) **(b)** Computer-generated XRD pattern for kassite based on the $CaSb_2O_6$ structure.

synthetic kassite were determined from the XRD pattern to be $a = 0.524(1)$, $b = 0.468(1)$, $c = 0.524(1)$ nm and $\beta = 120.0(1)°$ (equivalent to an orthorhombic cell with dimensions $a = 0.908$, $b = 0.468$, and $c = 0.524$ nm).

Not all of the hematite was removed by the sodium dithionite treatment, as indicated by the presence of a few hematite diffraction lines. The composition and thermal characteristics of the synthetic kassite were determined by EDX and DTA analysis, respectively. Our analyses confirmed the Russian results.

By using the Rietveld refinement program of Hill and Howard (1986), we compared the XRD pattern in Figure 4a to our proposed structure. A calculated pattern for the structure, shown in Figure 4b, is in reasonable agreement with the experimental pattern. The atomic positions for $CaSb_2O_6$ are not available, and so the positions used to generate the pattern in Figure 4b were those for the isostructural compound $PbSb_2O_6$ as given by Wyckoff (1965).

A Rietveld refinement of the kassite structure was attempted using the XRD pattern in Figure 4a. However, the slight distortion of the unit cell from hexagonal geometry meant that many reflections were unresolved, and so the effects of instrumental parameters (especially peak width) could not be distinguished from the effects of crystallographic parameters. A full structure refinement will undoubtedly require single-crystal X-ray measurements, but unfortunately crystals large enough for such work have not as yet been found.

DISCUSSION

Our experiments strongly suggest that kassite has a chemical formula of $CaTi_2O_4(OH)_2$ and a structure differing from that of $CaSb_2O_6$ by only a slight distortion from ideal hexagonal symmetry. This structure is closely related to that of lucasite, except that the *b* axis of kassite as determined by SAED is half that of the lucasite structure; however, the original Russian work does report a doubled *b* axis. In the structure with doubled *b* axis, the Ca atoms would be displaced from the ideal $CaSb_2O_6$ positions (sixfold coordination) to positions having eightfold coordination (see Nickel et al., 1987). As with the failure of Rietveld refinement, the true nature of the Ca coordination will only be resolved when crystals large enough for single-crystal X-ray diffraction are found.

The above conclusions for the structure of kassite are not in agreement with those of Evans et al. (1986). Given the results of our study, it would seem that the Russians did not necessarily intermix samples of kassite and cafetite. This leaves a dilemma as how to reconcile the conclusions of Evans et al. with our results and those of Kukharenko et al. (1965). It is known that kassite and cafetite coexist, and Figure 227 of Kukharenko et al. (1965) shows cafetite with a tangled-fiber morphology lying next to kassite with a blocky morphology. Interestingly, this figure is similar to the SEM photographs of Evans et al., who describe two types of kassite—platy rosettes and yellow spherules. The crystallographic work of Evans et al. was carried out only on the rosettes, and so it is possible that the mineral with the cafetite structure has a rosette or tangled-fiber morphology while kassite has the more blocky spherule morphology.

Evans et al. based their results not only on Fe content but also on crystal habit. Because of the nature of our sample we were unable to determine any morphological or crystal-habit properties of the kassite from Josephine Creek. We are unable to offer an explanation for the discrepancy between the crystal habit of the sample of Evans et al. (which we would label cafetite) and that of cafetite described by Kukharenko et al. (1965).

From the results of our study of kassite from Josephine Creek, we conclude that kassite and cafetite should not be distinguished by Fe content but rather by crystallographic properties. Even so, it seems that the status of kassite and the related mineral cafetite are destined to remain controversial until more specimens have been characterized.

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