THE AMERICAN MINERALOGIST, VOL. 49, MARCH–APRIL, 1964

ON THE DISTRIBUTION OF MINOR COMPONENTS DURING THE FORMATION OF MINERALS

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Abstract

The purpose of this paper is to point out the geochemical implications of distribution coefficient studies on coupled substitution in scheelite crystals. It is found that by changing the amounts of minor additions neodymium and niobium in calcium tungstate melts during the Czochralski growth of scheelite single crystals, either ion can be made to become more concentrated in the melt or in the crystal. Even though the results can be rationalized *a posteriori* on chemical grounds, it is clear that deductions as to magma composition made on the basis of mineral analyses will, in general, not be valid unless allowance is made for all the possible interactions among the chemical species present since these can dominate the customary factors of size, charge and electronegativity.

Introduction

The importance of Goldschmidt's (1937) work on trace element distribution is well established in the field of geochemistry, but, as in any other field, the rigid application of rules derived from experience is fraught with danger. The various rules of Goldschmidt for ion replacement appear to apply to some of the usual magma systems; however, their applicability is not as wide as might be expected from a perusal of textbook descriptions. In the present work, a simple system, consisting of scheelite ($CaWO_4$) with coupled substitution of neodymium and niobium, shows a variability in substitution behavior incompatible with Goldschmidt's rules.

Experimental Details and Discussion

The general technique for the growth of calcium tungstate crystals containing rate earth ions and the coupled substitution with alkali metal ions of the type $(Ca_{1-2x}{}^{2+}Nd_x{}^{3+}Na_x{}^{+})WO_4$ have been described in some detail (Nassau and Broyer, 1962; Nassau, in press; Nassau and Loiacono, in press). The most drastic effect, however, is observed with neodymium-niobium coupled substitution, which is equivalent, in the idealized case, to $(Ca_{1-x}{}^{2+}Nd_x{}^{3+})(W_{1-x}{}^{6+}Nb_x{}^{5+})O_4$. However, either neodymium or niobium can enter scheelite alone, presumbably by the formation of vacancies in Ca or in O sites as $(Ca_{1-3x}{}^{2+}Nd_{2x}{}^{3+})WO_4$ and $Ca(W_{1-2x}{}^{6+}Nb_{1x}{}^{5+})O_{4-x}$ as in the sodium case (Nassau and Loiacono, in press). It will be noted that Ca, Na and the Y type rare earths are related to each other by Goldschmidt's diagonal rule for ready isostructural substitution (Eitel, 1954), the same being true of Nb and W.

In Table 1 are listed the corresponding melt and crystal concentrations of neodymium and niobium as determined by x-ray spectrochemical analyses. Concentrations are expressed as atom per cent replacement of Ca or W atoms. The distribution (or partition) coefficient k gives the ratio of concentration of a given solute in the crystal to that in the melt. The estimated accuracy of the analyses is ±2%.

Examination of the k_{Nd} values of Table 1 shows that addition of niobium raises the distribution coefficient of neodymium above the value of 0.24 in the absence of Nb; under appropriate circumstances the direction of concentration even reverses, k exceeding unity. Increasing the concentration of Nd has been shown to reduce k_{Nd}, but not as drastically as changing the concentration of Nb (Nassau and Loiacono, in press).

TABLE 1.

Experiment No.		K536	L125	K614	L130
Atom % Nb	in melt	0	0.12	1.18	3.78
	in crystal	0	0.18	0.96	1.46
Atom % Nd	in melt	4.08	1.02	0.76	1.16
	in crystal	0.98	0.48	0.88	1.10
Ratio Nd/Nb	in melt	—	8.5	0.64	0.31
	in crystal	—	2.7	0.92	0.75
Distribution	k_{Nd}	0.24	0.47	1.16	0.95
Coefficients	k_{Nb}	—	1.50	0.81	0.39

An even more drastic effect is seen when variable amounts of niobium are added to a more or less constant $CaWO_4$:Nd melt, as in the last row of Table 1. Here the change in k_{Nb} is from 1.50 to 0.39, an almost fourfold change from concentrating in the crystal to concentrating in the melt.

An examination of both k and Nd/Nb values leads to a qualitative explanation. The low value of k_{Nd} in experiment K536 shows the entry of Nd^{3+} into the scheelite structure with vacancy compensation to be energetically unfavorable compared to normal Ca^{2+} entry. Coupled substitution of Nd and Nb appears to be close to $CaWO_4$ in energy, since experiment K614 shows that as the concentrations of Nd and Nb approach equality, both have k values not far from unity. Another way of expressing this tendency can be derived from the Nd/Nb values of Table 1. It is seen that a type of buffer action exists, the crystal maintaining a Nd/Nb value closer to unity than the melt. A more detailed report on the niobium compensation of rare earths in calcium tungstate will appear elsewhere.

It should incidentally be pointed out that in the case of the neodymium-alkali metals coupled substitution, Na has a larger effect on increasing k_{Nd} than any of the other alkali metal ions (Nassau, in press; Nassau and Loiacona, in press). This is presumably due to its better fit into the Ca site (0.95 Å in 0.99 Å) than either the larger or the smaller alkali metal ions, which again is not consistent with Goldschmidt's rules. A quantitative theory has been developed which fits the data for the Na and K cases in detail (Nassau, in press).

The implications for geochemistry are clear. For valid conclusions to be drawn about magma compositions from analyses of minerals, full allowance would have to be made for all the different chemical species present, since quite small variations in composition can change, not only the magnitude, but even the direction of the movement of minor components.

Analogous conclusions have been drawn by L. V. Tausson (1950) on the basis of the energy calculated for some of the substitutions observed in minerals. The present work provides experimental verification of these conclusions in a simple system of few components. The results are in a sense complimentary to the discussions of Goldschmidt (1937), Shaw (1953), and Ringwood (1955); they show, however, that the specific effects of size, charge and electronegativity can be dominated by a coupled substituting ion. Even though a reasonable explanation can be postulated for the observed behavior, it is clear that this could not have been deduced *a priori*.

ACKNOWLEDGMENT

The author wishes to thank S. M. Vincent and J. Kessler for the analytical results, G. M. Loiacono for experimental assistance, and J. B. MacChesney for helpful discussions.

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Manuscript received, August 26, 1963; accepted for publication, October 7, 1963.