

from  $-24.6$  to  $-36$  °C, indicating exceedingly saline brines (saturated NaCl solution freezes at  $-21$ °). Most inclusions suitable for filling-temperature determination homogenized at  $+71$ ° to  $+108$  °C. A small pressure correction must be added to obtain the trapping temperature.

Dolomite crystals from some of the same vugs contain large numbers of primary inclusions, many of which have leaked. Those that have not leaked had similar filling temperatures, but considerably lower salinities. Inclusions in a 4-cm cleavage fragment of calcite appeared to have similar gas/liquid ratios, but had still lower salinities (freezing temperatures  $-3$  to  $-5$  °C).

The significance of these data lies in the limitations they place on the choice of possible mechanisms of origin of these large deposits. This choice, in turn, may influence the success in prospecting for blind orebodies. There is general agreement that the deposits are Mississippi Valley type. Although the high salinities probably reflect solution of salts from the evaporite sequence to the south, the elevated temperatures seem to require deep circulation, perhaps through known faults in the underlying Precambrian. The densities of these brines, even at their elevated temperatures, are well above that of fresh, cold surface water, thus restricting the possible modes of circulation during ore deposition.

## ELECTRON PROBE STUDIES OF SOME CANADIAN TELLURIDE MINERALS

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As part of a broader study of telluride minerals from world wide localities, several Canadian specimens have been subjected to electron microprobe examination. The unique occurrences at Robb Montbray, Quebec, have proved most interesting, and it has been possible to confirm the suspected formula of frohbergite,  $\text{FeTe}_2$ . Frohbergite has also been found in association with petzite in specimens from Noranda, Quebec and Lindquist Lake, British Columbia. The enigmatic gold telluride, montbrayite,  $\text{Au}_2\text{Te}_3(?)$ , has been shown to contain essential Pb and Bi, formerly ascribed to impurities in the chemical analysis, and the association of this phase with calaverite,  $\text{AuTe}_2$ , has been noted. A new Pb-Ti telluride, probable formula  $(\text{Pb, Bi})_3\text{Te}_4$ , has been found as minute inclusions in chalcopyrite from Robb Montbray.

Specimens of petzite,  $\text{AuAg}_3\text{Te}_2$ , from Robb Montbray, Noranda-Kirkland Lake area, and isolated localities in western Canada have been shown to have a constant stoichiometric composition, while being extremely sensitive to the effect of electron bombardment. Hessite,  $\text{Ag}_2\text{Te}$ , is similarly constant in composition, but calaverite  $\text{AuTe}_2$  has a variable amount of silver.

The electron microprobe studies have clarified the range of variation of telluride mineral compositions, and in many respects confirmed earlier synthetic work.

## EXPERIMENTAL DETERMINATION OF THE STABILITY OF ALUMINOUS IRON BIOTITES

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Many natural biotites, contain more aluminum than biotites of the join phlogopite-annite. Phase relations of such biotites have been determined at 2 Kb pressure. Compositions lie on the join  $\text{K}_2\text{Fe}_6\text{Al}_2\text{Si}_8\text{O}_{20}(\text{OH})_4$ — $\text{K}_2\text{Fe}_{4.5}\text{Al}_{4.5}\text{Si}_8\text{O}_{20}(\text{OH})_4$  with some octahedral vacancies.

At  $f_{O_2}$  values of Ni-NiO the most aluminous biotite coexisting with quartz decomposes to Fe-cordierite + sanidine + magnetite<sub>ss</sub> at  $680 \pm 5^\circ\text{C}$  and reacts with Fe-cordierite to form magnetite<sub>ss</sub> + hercynite<sub>ss</sub> + sanidine at  $685 \pm 5^\circ\text{C}$ . The upper stability of less aluminous biotites lies between these temperatures and the annite decomposition ( $630^\circ\text{C}$ ). Three invariant points, each involving seven of the eight phases Al-biotite, almandine, Fe-cordierite, magnetite<sub>ss</sub>, hercynite<sub>ss</sub>, sanidine, quartz, and vapor, exist near  $700^\circ$  and  $f_{O_2}$  values near those of the QFM buffer. They are (Sa), (Fe-Cord.), and (Mte). The corresponding invariant point for annite lies on QFM at  $680 \pm 10^\circ\text{C}$ . Four reactions which limit the stability field of Al-biotite radiate from these invariant points to lower  $f_{O_2}$  values. They intersect the graphite-methane buffer curve as follows: Al-biotite + quartz + Fe-cordierite  $\rightleftharpoons$  almandine + sanidine ( $665 \pm 5^\circ\text{C}$ ); Al-biotite + quartz  $\rightleftharpoons$  almandine + fayalite + sanidine ( $685 \pm 5^\circ\text{C}$ ); Al-biotite + Fe-cordierite  $\rightleftharpoons$  almandine + hercynite + sanidine ( $>665$  and  $>730^\circ\text{C}$ ); Al-biotite + almandine  $\rightleftharpoons$  fayalite + hercynite<sub>ss</sub> + sanidine ( $>800^\circ\text{C}$ ). This contrasts with the reaction annite + quartz  $\rightleftharpoons$  fayalite + sanidine at  $610 \pm 10^\circ\text{C}$  on the same buffer curve. Al-biotite data have been combined with almandine data and staurolite data to elucidate the metamorphism of pelitic schists.

Al-biotites of undersaturated environments remain stable to higher temperatures. The reaction Al-biotite  $\rightleftharpoons$  hercynite<sub>ss</sub> + magnetite<sub>ss</sub> + sanidine + leucite was located  $810 \pm 10^\circ\text{C}$  on the Ni-NiO buffer.

## NONSTOICHIOMETRIC PHASE CHANGES IN SPHALERITE AND WURTZITE

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Hydrothermal experiments in concentrated NaOH solutions demonstrate that sphalerite and wurtzite coexist as a univariant function of  $f_{S_2}$  and temperature at constant pressure. This relationship has been followed from  $460^\circ$  to  $520^\circ\text{C}$  and 4,000 to 9,000 psi. Calculated  $f_{S_2}$  at  $500^\circ\text{C}$  and 7500 psi is  $10^{-9}$  atm. Direct determination of  $f_{S_2}$  along the univariant curve at high temperatures and 1 atmosphere pressure made by passing  $\text{H}_2$  +  $\text{H}_2\text{S}$  gas mixtures over ZnS powder gave values of  $10^{-5}$  atm at  $890^\circ\text{C}$  and about  $10^{-6.8}$  atm at  $700^\circ\text{C}$ .

From experiments up to  $700^\circ\text{C}$  in NaOH solutions, only two wurtzite polytypes— $2H$  and  $4H$ —were identified by single crystal x-ray methods. All photographs show considerable diffuse streaking probably due to stacking disorders. The transition from the  $2H$  to the  $4H$  polytype is sharply defined at  $553 \pm 2^\circ\text{C}$  in 15 molal and  $560 \pm 2^\circ\text{C}$  in 6.2 molal NaOH. This demonstrates a thermodynamic control on wurtzite polytypism as a function of  $f_{S_2}$  and temperature.

These experiments show that phase changes in zinc sulfide are accompanied by composition change. Wurtzite is sulfur-deficient relative to sphalerite; therefore, these minerals are not true polymorphs. Similarly, the  $4H$  polytype contains less sulfur than the  $2H$  polytype. Published analyses indicate that the total range of nonstoichiometry is about 1 mole per cent sulfur.

## COVARIANCE ANALYSIS OF K-Rb FRACTIONATION TRENDS

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Rb concentrations in rocks and meteorites are roughly proportional to the K content. Recent careful studies indicate a marked divergence of opinion as to whether the ratio K/Rb (a) remains constant, or (b) decreases steadily throughout magmatic differentiation. All authors agree that low ratios characterize many late-stage magmatic products.