At f_{O_2} values of Ni–NiO the most aluminous biotite coexisting with quartz decomposes to Fe-cordierite + sanidine + magnetite$_{ss}$ at 680 ± 5 °C and reacts with Fe-cordierite to form magnetite$_{ss}$ + hercynite$_{ss}$ + sanidine at 685 ± 5 °C. The upper stability of less aluminous biotites lies between these temperatures and the annite decomposition (630 °C). Three invariant points, each involving seven of the eight phases Al–biotite, almandine, Fe–cordierite, magnetite$_{ss}$, hercynite$_{ss}$, sanidine, quartz, and vapor, exist near 700° 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 ± 10 °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 ± 5 °C); Al–biotite + quartz $\rightleftharpoons$ almandine + fayalite + sanidine (685 ± 5 °C); Al–biotite + Fe–cordierite $\rightleftharpoons$ almandine + hercynite + sanidine (>665 and >730 °C); Al–biotite + almandine $\rightleftharpoons$ fayalite + hercynite$_{ss}$ + sanidine (>800 °C). This contrasts with the reaction annite + quartz $\rightleftharpoons$ fayalite + sanidine at 610 ± 10 °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$_{ss}$ + magnetite$_{ss}$ + sanidine + leucite was located 810 ± 10 °C on the Ni–NiO buffer.

NONSTOICHIOMETRIC PHASE CHANGES IN SPHALERITE AND WURTZITE

S. D. Scott and H. L. Barnes

Materials Research Laboratory and Department of Geochemistry and Mineralogy, The Pennsylvania State University, University Park, Pennsylvania

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° to 520 °C and 4,000 to 9,000 psi. Calculated f_{S_2} at 500 °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 H_2 + H_2S gas mixtures over ZnS powder gave values of 10^{-5} atm at 890 °C and about $10^{-6.8}$ atm at 700 °C.

From experiments up to 700 °C in NaOH solutions, only two wurtzite polytypes—2*H* and 4*H*—were identified by single crystal *x*-ray methods. All photographs show considerable diffuse streaking probably due to stacking disorders. The transition from the 2*H* to the 4*H* polytype is sharply defined at 553 ± 2 °C in 15 molal and 560 ± 2 °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 4*H* polytype contains less sulfur than the 2*H* polytype. Published analyses indicate that the total range of nonstoichiometry is about 1 mole per cent sulfur.

COVARIANCE ANALYSIS OF K–Rb FRACTIONATION TRENDS

D. M. Shaw

Department of Geology, McMaster University, Hamilton, Ontario

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.

Analysis of K–Rb covariance in 21 igneous and quasi-igneous suites of high-quality published data resolved the controversy and helped define three principal trends. The first is characterized by near-constancy of the ratio in each of 12 suites, with an overall average of 263, but slight decrease as K increases; this main trend extends from 0.002–8 per cent K and 0.1–500 ppm Rb. The second is a trend of decreasing K/Rb ratios from more tha 3,500, merging with the main trend, and shown by all and only by oceanic tholeiites (and achondrites). The third is the pegmatitic-hydrothermal trend of extreme Rb concentration while K remains constant in the range 3–10 per cent or may even decrease.

These trends depend on (a) phase petrology, since K and Rb partition ratios differ with mineral species, and (b) presence or absence of a fluid phase, in which Rb concentrates preferentially to K. Several aspects of these trends, however, are obscure.

K/Rb ratios provide a criterion for certain kinds of metasomatic replacement.

THE COMPOSITION OF THE CANADIAN PRECAMBRIAN SHIELD AND THE UPPER MANTLE, WITH PARTICULAR REFERENCE TO U, Th, AND K

D. M. Shaw

Department of Geology, McMaster University, Hamilton, Ontario

A new estimate of the composition of the Canadian Precambrian Shield is: SiO_2, 64.93; TiO_2, 0.52; Al_2O_3, 14.63; Fe_2O_3, 1.36; FeO, 2.75; MnO, 0.07; MgO, 2.24; CaO, 4.12; Na_2O, 3.46; K_2O. 3.10; P_2O_5, 0.15; H_2O^+, 0.79; H_2O^-, 0.13; CO_2, 1.28; S, 0.06; Cl, 0.01; F, 0.05; C, 0.02, all in per cent and Be, 1.3; Ga, 14; Cr, 99; V, 53; Li, 22; Ni, 23; Co, 21; Cu, 14; Zr, 400; U, 2.5; Th, 10.3; Sr, 340; Ba, 1070; Rb, 118, all in ppm. This estimate is based on numerous analyses of composite and individual rocks from northern Quebec–Ungava, Baffin Island, southwestern Quebec, northeastern Alberta, northern Saskatchewan, and northwestern Ontario. Differences between regions are striking, especially for trace elements.

The concentrations of U, Th, and K, taken as typical of the whole continental crust, could have been produced by differentiation of an achondritic earth, leaving concentrations suitable for simulating the sub-oceanic and sub-continental upper mantles from various possible mixtures of dunite, eclogic, oceanic tholeiite, and oceanic alkalic basalt. The achondritic parent was assumed to contain 0.05 ppm U, 0.20 ppm Th, and 0.035 per cent K; its heat production, averaged over the whole earth surface, is 3.19×10^{-6} cal/cm²/sec, which is higher by a factor of 2 than the observed average. Alternative models, based on the average chondrite or the average type I carbonaceous chondrite, have suitable heat production but unsatisfactory compositions.

X-RAY DIFFRACTION AS A STRATIGRAPHIC TOOL IN THE PLEISTOCENE OF NORTHERN VERMONT AND SOUTHEASTERN QUEBEC

W. Shilts

Department of Geology, Syracuse University, Syacruse, New York

X-ray diffraction patterns of silt-clay reflect provenance changes in the late Wisconsin drift of northern Vermont. Comparing the ratios derived from the diffraction line intensity of chlorite (7.16 Å) divided by the intensity of quartz (4.26 Å), a definite response to changing drift lithologies was noted. Chlorite ratios drop sharply on the down-ice side of the contact of high chlorite, Green Mountain schists with low chlorite limestones and slates. For multiple till sections near Sherbrooke in southeastern Quebec, tills with northwest fabric were consistently lower in chlorite/quartz ratio than those with northeast fabric. Illite/quartz ratios are also consistently higher in northeast tills than in northwest, *x*-ray diffraction confirms fabric and mega-lithology data obtained independently by McDonald.