

A Cautionary Tale of Spinel Peridotite Thermobarometry: an Example from Xenoliths of Kozákov Volcano, Czech Republic

Gordon L. MEDARIS¹, Jr., Herbert F. WANG¹, John H. FOURNELLE¹, John H. ZIMMER¹ and Emil JELÍNEK²

¹ Department of Geology and Geophysics, University of Wisconsin, Madison, WI, 53706, United States

² Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, 128 43 Praha 2, Czech Republic

ABSTRACT. Protogranular and equigranular spinel lherzolite xenoliths are abundant in basanite lavas at the Neogene Kozákov volcano, located in the northern Czech Republic near the Lužice Fault, which marks the eastern end of the Ohře Rift. Two-pyroxene thermometry yields 835^o–1,045^oC for protogranular, 680^o–1,065^oC for equigranular, and 700^o–735^oC for two composite samples (at P = 15 kbar). Careful analysis of Ca in olivine and application of the Ca-in-olivine barometer demonstrate that this barometer is unreliable and that geotherms constructed by such application are spurious. The Kozákov basanites erupted at 5 Ma, but were preceded by major regional volcanism at 30 to 35 Ma, and the thermal evolution of the lithosphere has been calculated from an underplating model, based on geological and geophysical data. The thermal scenario implies that mantle at shallow depths was heated to higher temperatures and cooled faster than was mantle at deeper levels, and differences in the characteristics of pyroxene exsolution lamellae in shallower xenoliths compared to those in deeper xenoliths are consistent with such an implication. Forcing the xenolith two-pyroxene temperatures onto the Model geotherm at 5 Ma, the time of eruption, indicates that the xenoliths were derived from depths of 32 to 70 km, which is consistent with phase petrology and the depth of the crust–mantle boundary, and that the sub-Kozákov lithosphere has a layered structure, in which protogranular lherzolite at depths of 45 to 68 km is sandwiched between shallower and deeper layers of equigranular lherzolite.

KEY WORDS: spinel-peridotite thermobarometry, spinel lherzolite xenoliths, Kozákov.

Geological setting

Peridotite xenoliths are abundant in the nepheline basanite lava flows of Kozákov volcano, which erupted at 4–6 Ma (Šibrava and Havlíček 1980) and is located about 7 km east of Turnov, immediately east of the NW-trending Lužice Fault, which forms the northeastern boundary of the Ohře Graben. Kozákov lavas are rich in upper mantle material; peridotite xenoliths comprise 2–3% of the lavas, and xenocrystic olivine, another 7–8%. The xenoliths described in this study were collected from quarries at Chuchelna, Slap, and Smrčí, which are located within 4 km of each other.

Petrography

Peridotite xenoliths are spheroidal to ellipsoidal in shape, are commonly 6–10 cm in diameter (rarely up to 70 cm), and consist predominantly of spinel lherzolite, with subordinate harzburgite, dunite, and composite lherzolite/pyroxenite. Two textural varieties of lherzolite occur at Kozákov: coarse- to very coarse-grained protogranular lherzolite (olivine grains 4 mm to 2 cm in diameter), in which spinel occurs only in symplectitic intergrowth with orthopyroxene and clinopyroxene, and medium-grained equigranular lherzolite (olivine, 1 to 4 mm in diameter), which contains discrete, intergranular spinel. No porphyroclastic peridotite has been found so far at Kozákov. In both protogranular and equigranular xenoliths, small amounts of very fine-grained silicates are present locally at spinel-pyroxene boundaries, as a result of incipient partial fusion.

Reconstructed bulk chemical compositions of spinel-pyroxene symplectite domains in protogranular lherzolite are consistent with symplectite formation by the reaction of pre-existing garnet with matrix olivine (Medaris et al. 1997), and garnet-olivine reaction was probably promoted by heating during Neo-

gene volcanism, when basaltic magmas may have underplated the continental crust.

Mineral Chemistry

Mineral compositions were determined by means of a Cameca SX50 microprobe, using an acceleration voltage of 15 kV, a beam current of 20 nA, a suite of analysed natural minerals as standards, and the PAP data reduction program. Special attention was paid to the analysis of Ca in olivine; for the analytical conditions and Ca standard (wollastonite) used, a counting time of 300 seconds yields a minimum detection limit of 0.008 wt.% CaO and a precision of 3%, based on counting statistics.

The Kozákov xenoliths are typical of Group I upper mantle xenoliths (Frey and Prinz 1978), consisting of magnesian olivine and orthopyroxene, Cr-diopside, and aluminous spinel. Each mineral species is homogeneous within a given xenolith, and no significant differences in composition were found between cores and rims of grains, except locally in the vicinity of domains where incipient partial melting occurred, and locally at the margins of olivine grains, where there is an increase in Ca. The forsterite content of olivine in lherzolite ranges from 90.2 to 91.7 mol.%, and in composite xenoliths, from 88.2 to 89.1 mol.% (Fig. 1). The positive correlation between mol.% forsterite in olivine and Cr-content of spinel (Fig. 1) is due to the residual nature of the xenolith bulk compositions, reflecting variable degrees of melt extraction. Olivine in equigranular samples spans a greater compositional range than that in protogranular samples, as do pyroxene and spinel.

The mg-number of orthopyroxene ranges from 90.4 to 92.0 in lherzolite and from 88.2 to 89.4 in composite samples. The Al₂O₃ and Cr₂O₃ contents in orthopyroxene are 1.74–5.88 wt.% and 0.21–0.80 wt.%, respectively, corresponding to different

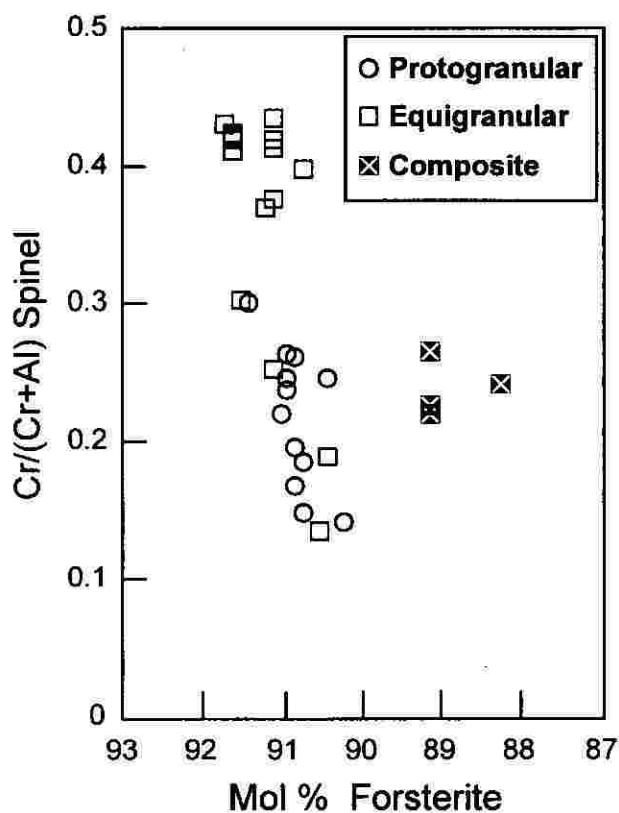


Fig. 1. The correlation between mol % forsterite in olivine and Cr content of spinel for spinel lherzolite xenoliths from Kozákov.

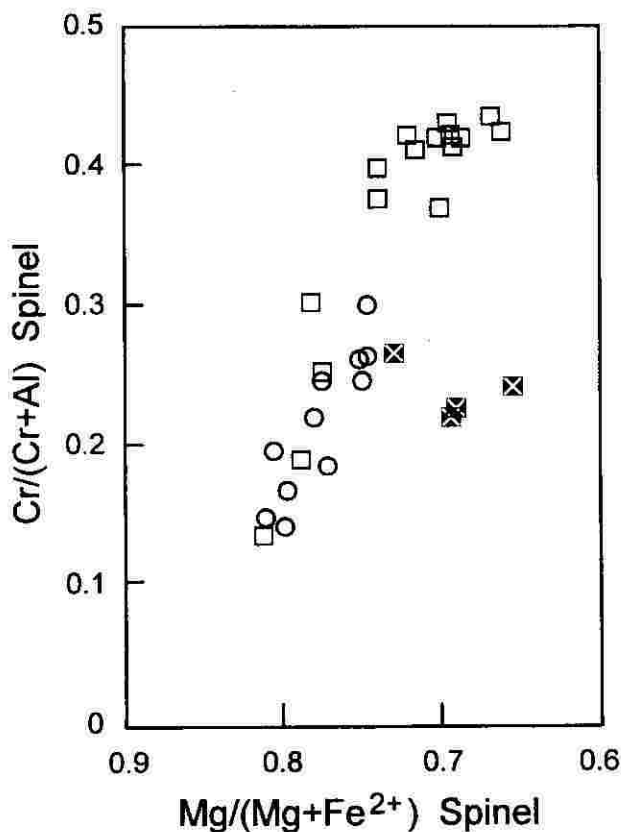


Fig. 3. The compositional trend for spinel (*mg* vs. *cr* - number) in the Kozákov xenoliths.

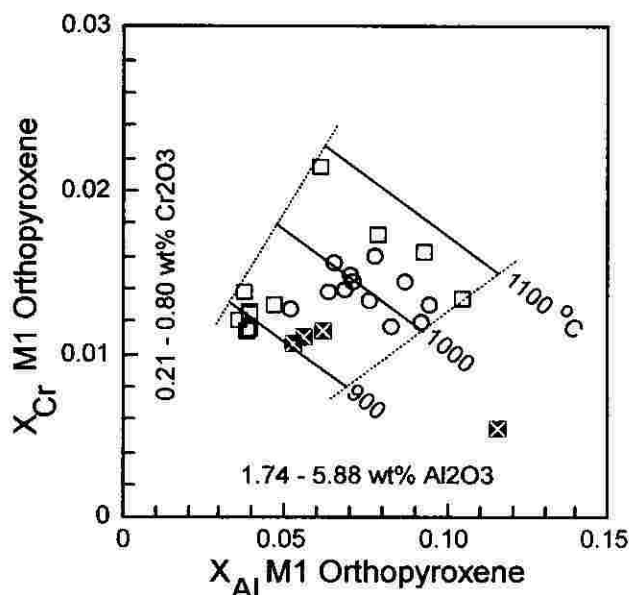


Fig. 2. Al vs. Cr content in orthopyroxene of spinel lherzolite xenoliths from Kozákov. The isotherms (solid lines) are based on Al-in orthopyroxene thermometer of Witt-Eickschen and Seck (1991).

equilibration temperatures, as illustrated by the isotherms in Fig. 2, which are based on the Al in orthopyroxene thermometer (Witt-Eickschen and Seck 1991). The compositional variation in *Cr-diopside* (not shown) is comparable to that in orthopyroxene, with *mg*-number ranging from 89.4 to 95.3 and Al_2O_3 and Cr_2O_3 contents of 2.03–6.89 and 0.30–1.80 wt.%, respectively.

The compositional trend for *spinel* is typical for that in mantle xenoliths, with a range in *mg*-number from 66.1 to 81.2 and in *cr*-number from 13.1 to 42.1 in lherzolite, and *mg*-number from 65.3 to 73.0 in composite samples (Fig. 3). As is the case with olivine and pyroxenes, the composition of spinel in equigranular xenoliths overlaps with that in proto-granular xenoliths and has a wider range of variation.

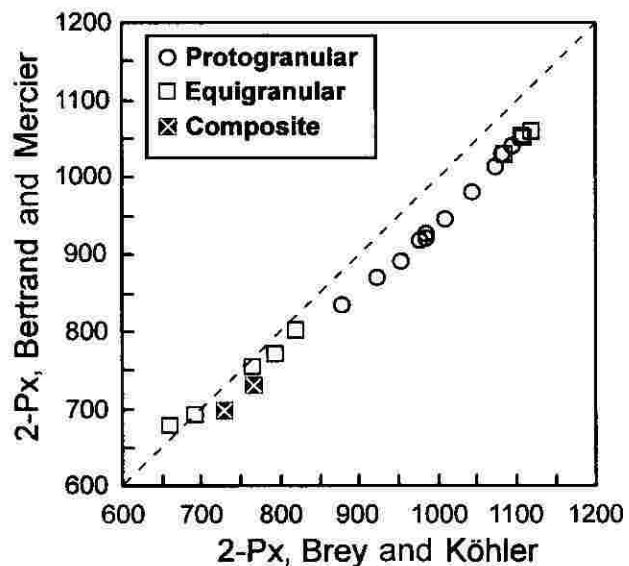


Fig. 4. Comparative thermometry (two-pyroxene thermometers) for Kozákov xenoliths. ($T^{\circ}C$ at 15 kbars).

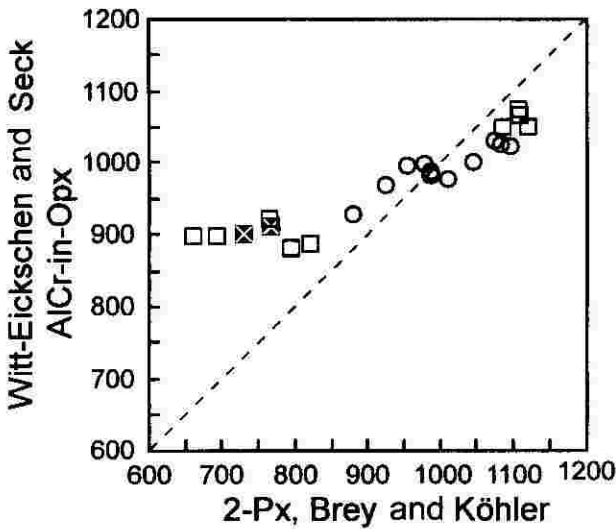


Fig. 5. Comparative thermometry of two-pyroxene vs. Al-in orthopyroxene thermometers for Kozákov xenoliths ($T^{\circ}\text{C}$ at 15 kbars).

Geothermometry

Temperatures have been calculated (at $P = 15$ kbar) for 11 protogranular, 9 equigranular, and 2 composite xenoliths by two versions of the two-pyroxene thermometer (Bertrand and Mercier 1985; Brey and Köhler 1990), the Al-in-orthopyroxene thermometer (Witt-Eickschen and Seck 1991), and the olivine-spinel Mg- Fe^{2+} exchange thermometer (Ballhaus et al. 1991). In general, there is good agreement among the different methods, reflecting the attainment and preservation of equilibrium among most elements in coexisting olivine, orthopyroxene, clinopy-

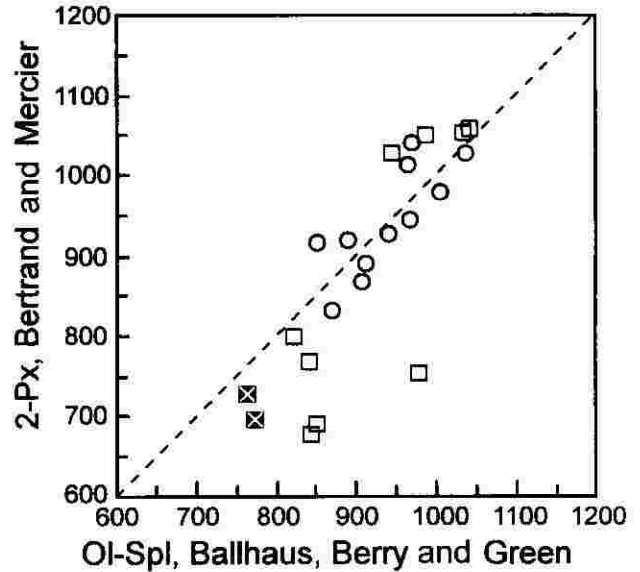


Fig. 6. Comparative thermometry of two-pyroxene vs. olivine-spinel thermometers for Kozákov xenoliths ($T^{\circ}\text{C}$ at 15 kbars).

roxene, and spinel. The wide range of temperatures, from ~ 650 to $\sim 1,100^{\circ}\text{C}$, implies that the xenoliths were extracted from a wide range of depths.

Results from the Brey and Köhler (1990) calibration of the two-pyroxene thermometer are in excellent correspondence with those of the Bertrand and Mercier (1985) calibration at temperatures below 850°C and are uniformly $\sim 50^{\circ}\text{C}$ higher at higher temperatures (Fig. 4). Temperatures from the empirical Al-in-orthopyroxene thermometer are in good agreement with those from the two-pyroxene thermometer above $\sim 900^{\circ}\text{C}$, but diverge increasingly at lower temperatures (Fig. 5), perhaps reflecting quenching of the slow-diffusing element, Al, in orthopyroxene at $\sim 900^{\circ}\text{C}$ (see below for a discussion of the thermal history of the xenolith suite). Good agreement is also found between the

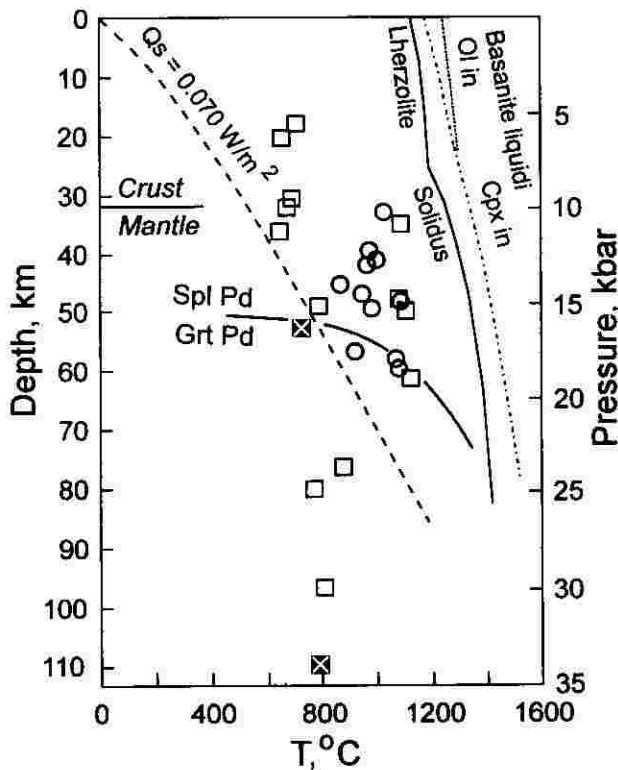


Fig. 7. Kozákov xenoliths in temperature - depth - pressure plot. Iterative sections: two-pyroxene thermometer and Ca-in olivine barometer (Köhler and Brey, 1990).

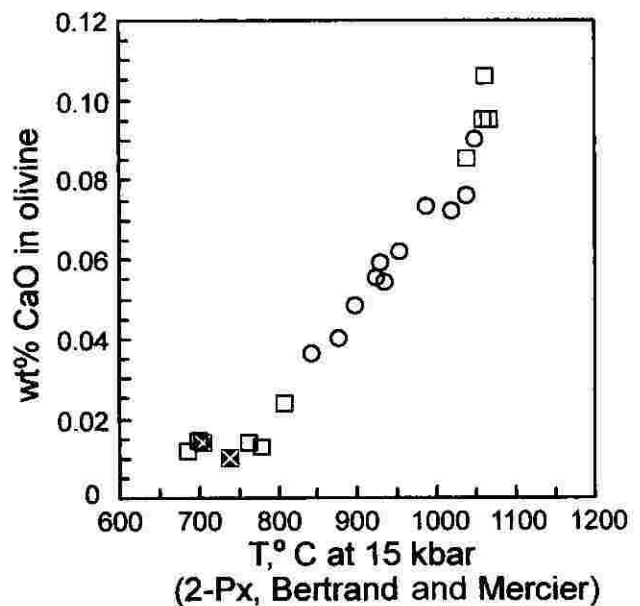


Fig. 8. The correlation between CaO content in olivine and temperature (two-pyroxene thermometer) for Kozákov spinel lherzolite xenoliths.

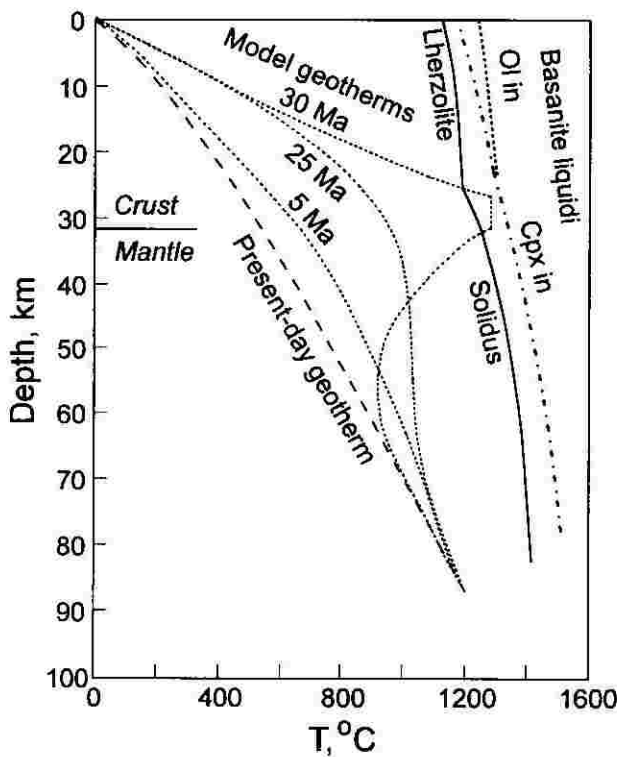


Fig. 9. The thermal evolution of lithosphere beneath Kozákov volcano (underplating model). Calculation of the geotherms – see text for explanation and discussion).

two-pyroxene thermometer and the olivine–spinel thermometer, except for three lower temperature equigranular samples (Fig. 6).

Geobarometry

Currently, the only method for estimating pressure in spinel lherzolites is based on the Ca content of olivine (Köhler and Brey 1990). Accordingly, pressures and temperatures have been calculated for the Kozákov xenoliths by an iterative solution to the Ca-in-olivine barometer and the Brey and Köhler two-pyroxene thermometer. The results are widely scattered and do not lie along a geotherm; higher temperature samples cluster between 10 and 20 kbar, and lower temperature samples range from 6 to 34 kbar (Fig. 7). Such scatter has been reported in other xenolith suites and has been attributed to loss of Ca from olivine in the “poorly behaved” samples (Köhler and Brey 1990). However, there is no indication of Ca loss from olivine in any of the Kozákov samples; on the contrary, Ca contents are uniform in the cores of olivine grains, but locally increase within 50 micrometers of grain margins (even in grains distant from clinopyroxene and therefore unaffected by fluorescence), due to late-stage addition of Ca related to eruptive processes. In addition, the Ca content of olivine cores shows an excellent positive correlation with temperature calculated by the two-pyroxene thermometer (Fig. 8), indicating that the Ca content in olivine might be an effective geothermometer, if not a reliable geobarometer. The data from the Kozákov xenoliths indicate that the Ca-in-olivine barometer is incorrect and its application will produce spurious results.

Thermal model

The lowermost crust beneath the Kozákov volcano has a seismic velocity of 6.9 km/sec (Čermák 1989), which may repre-

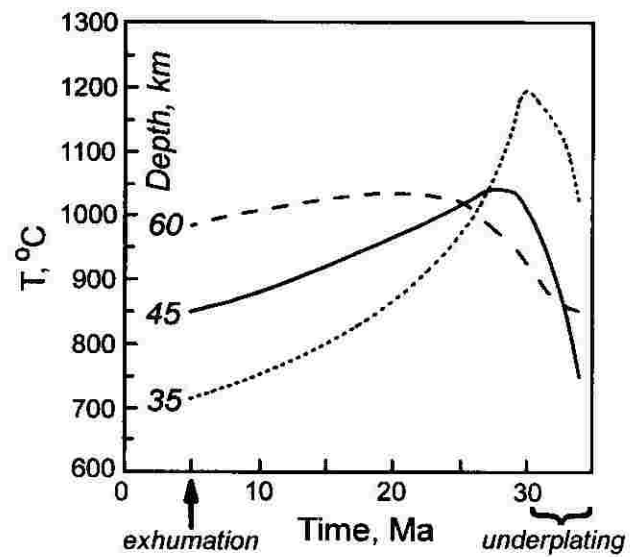


Fig. 10. Thermal histories for mantle beneath Kozákov volcano.

sent the crystallized products of basic magmas that underplated the crust during the culmination of Neogene magmatism in the Ohře Graben and adjacent areas. The thermal evolution of lithosphere beneath Kozákov volcano has been calculated for an underplating scenario, in which a 5-km thick layer of basaltic magma at 1,300°C accumulated at the base of the crust during a 5 million year period, between 35 and 30 Ma. The present-day geotherm, in which the surface heat flow is 70 mW/m² (Čermák et al. 1991), was taken to be the initial geotherm at 35 Ma. The resulting geotherms at 30, 25, and 5 Ma are shown in Fig. 9. A significant implication of the thermal model is that shallow lithosphere was heated to higher temperatures and cooled faster than deeper lithosphere, as illustrated in Fig. 10 for depths of 35, 45, and 60 km. Predicted cooling rates for the 10 m.y. period following maximum heating at depths of 35, 45, and 60 km are about 34°, 10°, and 3°/m.y., respectively. Such cooling rates are consistent with the different features of exsolution lamellae in orthopyroxene from lower temperature compared to higher temperature xenoliths. Exsolution lamellae in lower temperature samples are abundant and relatively thin and diffuse, compared to those in higher temperature samples, which are uncommon and relatively thick and sharply defined.

Spinel lherzolites, paleogeotherms and xenolith extraction depths

At present there is no viable geobarometer for spinel lherzolite xenoliths, and paleogeotherms can not be reconstructed directly from them. However, maximum pressures for spinel lherzolites can be determined from the Cr content of spinel (O'Neill 1981), and such values can be used to place constraints on paleogeotherms. Temperatures and maximum pressures for the Kozákov spinel lherzolite xenoliths have been calculated by a combination of the two-pyroxene thermometer (Bertrand and Mercier 1985) and spinel “barometer” (O'Neill 1981), yielding maximum pressures from 19.5 to 27.2 kbar (Fig. 11). Although these pressures are only maxima, they are useful in constraining the eruptive geotherm to lie at pressures less than, or equal to, those of the xenolith suite, because otherwise, garnet should be stable in some lherzolite samples. Xenoliths that contain the most aluminous spinel are the most effective in constraining the geotherm, because they yield the lowest maximum pressures.

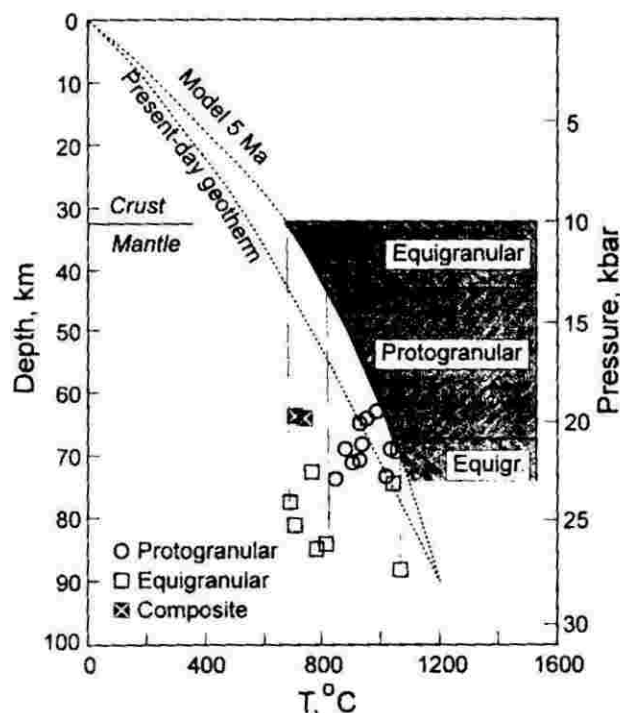


Fig. 11. Temperature–depth–pressure conditions for spinel lherzolite xenoliths from Kozákov (see text for discussion).

Considering the effect of pressure on the two-pyroxene thermometer (shown by the three thin solid lines in Fig. 11) and forcing the xenolith two-pyroxene temperatures onto the Model geotherm at the time of eruption, 5 Ma (the heavy curve in Fig. 11), indicate that the Kozákov xenoliths were extracted from a range in depth of 32 to 70 km, which is consistent with phase petrology and the position of the crust–mantle boundary, i.e., all the xenoliths lie in the spinel field and all are situated in the mantle.

Conclusions

Paleogeotherms based on the Ca content of olivine in spinel lherzolite xenoliths are spurious and lead to erroneous interpretations of lithospheric thermal evolution. However, the maximum pressures of spinel lherzolite xenoliths, determined by spinel compositions, place constraints on the possible configurations of paleogeotherms. In addition, given a viable thermal model and estimates of xenolith temperatures, extraction depths can be inferred by forcing the xenoliths onto a model geotherm at the time of eruption.

A thermal model based on Neogene underplating and heating is consistent with the estimated temperatures and maximum pressures of the Kozákov spinel lherzolite xenoliths. The xenoliths were derived from depths of 32 to 70 km, and it appears that the sub-Kozákov lithosphere has a layered structure, in which protogranular lherzolite is located at depths of 45 to 68 km, sandwiched between deeper and shallower layers of equigranular lherzolite (Fig. 11). Judging from olivine and spinel compositions, the upper layer of equigranular lherzolite is more depleted than the protogranular lherzolite and deeper layer of equigranular lherzolite. It has been previously suggested that

the protogranular lherzolite was emplaced as a slab of metastable garnet peridotite into the upper mantle during Variscan tectonic convergence and imbrication and that Neogene heating promoted the reaction of garnet and olivine to form spinel–pyroxene symplectite (Medaris et al. 1997). Chemical and isotopic investigations of the Kozákov xenolith suite are underway, in order to further an understanding of the geochemical and thermal evolution of central European subcontinental lithosphere.

References

- BALLHAUS C., BERRY R.F. and GREEN D.H. 1991a. High pressure experimental calibration of the olivine–orthopyroxene–spinel oxygen geobarometer: implications for the oxidation state of the upper mantle. *Contrib. Mineral. Petrol.*, 107, 27–40.
- BALLHAUS C., BERRY R.F. and GREEN D.H. 1991b. Erratum: High pressure experimental calibration of the olivine–orthopyroxene–spinel oxygen geobarometer: implications for the oxidation state of the upper mantle. *Contrib. Mineral. Petrol.*, 108, 384.
- BERTRAND P. and MERCIER J.C.C. 1985. The mutual solubility of coexisting ortho- and clinopyroxene: toward an absolute geothermometer for the natural system?. *Earth Planet. Sci. Lett.*, 76, 109–122.
- BREY G.P. and KÖHLER T. 1990. Geothermobarometry in four-phase lherzolites. II. New thermobarometers and practical assessment of existing thermobarometers. *J. Petrol.*, 31, 1352–1378.
- ČERMÁK V. 1989. Crustal heat production and mantle heat flow in Central and Eastern Europe. *Tectonophysics*, 9, 195–215.
- ČERMÁK V., KRÁL M., KRESL M., KUBÍK J. and ŠAFANDA J. 1991. Heat flow, regional geophysics, and lithosphere structure in Czechoslovakia and adjacent parts of Central Europe. In ČERMÁK V. and RYBACH L. (eds.): *Terrestrial Heat Flow and Lithosphere Structure*, 133–165. Springer Verlag, Berlin.
- FREY F.A. and PRINZ M. 1978. Ultramafic inclusions from San Carlos, Arizona: petrologic and geochemical data bearing on their petrogenesis. *Earth Planet. Sci. Lett.*, 38, 129–176.
- KÖHLER T.P. and BREY G.P. 1990. Calcium exchange between olivine and clinopyroxene calibrated as a geothermobarometer for natural peridotites from 2 to 60 kb with applications. *Geochim. Cosmochim. Acta*, 54, 2375–2388.
- MEDARIS L.G. Jr., FOURNELLE J.H., WANG H.F. and JELÍNEK E. 1997. Thermobarometry and reconstructed chemical compositions of spinel–pyroxene symplectites: evidence for pre-existing garnet in lherzolite xenoliths from Czech Neogene lavas. *Russian Geol. Geophys.*, 38, 277–286.
- O'NEILL H.St.C. 1981. The transition between spinel lherzolite and garnet lherzolite, and its use as a geobarometer. *Contrib. Mineral. Petrol.*, 77, 185–194.
- ŠIBRAVA V. and HAVLÍČEK P. 1980. Radiometric age of Pliocene–Pleistocene volcanic rocks of the Bohemian Massif. *Věst. Ústř. Úst. geol.*, 55, 129–139.
- WITT-EICKSCHEN G. and SECK H.A. 1991. Solubility of Ca and Al in orthopyroxene from spinel peridotite: an improved version of an empirical geothermometer. *Contrib. Mineral. Petrol.*, 106, 431–439.