EQUILIBRIUM CONDITIONS REVISITED FOR LESOTHO KIMBERLITES

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Ever since the first thermobarometers for peridotites have been proposed (Boyd, 1973; Wood and Banno, 1973), mantle models established from petrological/petrochemical studies are based on one critical parameter, the temperature estimates inferred from clinopyroxene solid-solution toward pure enstatite. Major improvements in thermobarometry have since consisted in more precise analyses, better controlled experiments, study of synthetic systems of intermediate complexity and more sophisticated solution models. However, clinopyroxene still provides the corner stone to the whole strategy aimed at determining equilibrium conditions of mantle rocks and, in particular, of the peridotites torn off the archean upper mantle and brought to the surface by kimberlites. Meanwhile, more and more contributors challenge directly or indirectly what may now be only considered as a postulate. Does such clinopyroxene represent at all the mantle equilibrium conditions since, very often, it appears to be a secondary phase related to metasomatism?

HARZBURGITES *vs* LHERZOLITES

The archean upper mantle sampled by kimberlites has long been recognized as comprising a thick sequence of harzburgites with some lherzolites at its base, whichever genetic interpretation has been given either of the relative chemistries (phase and modal compositions) or of the associated textural differences (coarse vs sheared). This description is petrographic and, as such, obeys the I.U.G.S. recommendations on nomenclature (Streckeisen, 1973) which sets the limit between rock types to a "magic" 10% of clinopyroxene (though many committee members advocated a lower cut-off value in better agreement with natural modes).

In terms of phase equilibria, this definition is irrelevant: in thermodynamics, what is important is the variance of the system, that is whether a mineral phase is present or not (however minute its concentration may be) and, if it is, whether it is in equilibrium or not. According to this perception, many harzburgites (IUGS-wise) with only very little clinopyroxene are referred to as lherzolites by some authors. Beyond this semantic debate, the very

nature of the peridotite that may represent the archean upper mantle is at stake.

Some now well-documented peridotites have garnets of subcalcic compositions (e.g. Boyd et al., 1993) which clearly show that they must have been clinopyroxene-free at the time garnet was equilibrated. Whenever some clinopyroxene is found in such xenoliths, this phase must thus have formed later through metasomatism, whichever the pyroxene composition may be.

Other peridotites with garnets of calcic composition which suggests that some clinopyroxene did originally coexist at equilibrium, show variable amounts of this phase, so rock types may be described either as harzburgites or lherzolites (IUGS-wise). However, in most samples, from Thaba Putsoa and Letseng-la-Terae, textural relations point to its secondary nature: association with phlogopite and spinel, symplectites related or not to garnets, crystallization in healed microfractures. Even the primary nature of many garnets appears dubious as this phase show inclusions of clinopyroxene and spinel with relations eventually evolving to macrosymplectites. Geochemical data on matrix clinopyroxene in apparent textural "equilibrium" fall into two groups, both of which appear clearly related to the metasomatic fluids of PIC and MARID types (see companion paper by Coussaert et al.). As for garnets, they show variable patterns unrelated to the clinopyroxene compositions. Such data confirm that the observed olivine-orthopyroxene-clinopyroxene-garnet assemblies cannot be regarded as being in thermodynamic equilibrium. Hence, classic geothermobarometers may not be used to model upper-mantle conditions, at least without some external control.

BACK TO THE BASIC PHASES: OL AND OPX

Unlike the classic opposition between spinel peridotites in basalts and garnet peridotites in kimberlites, the latter also offer a large variety of garnet-free spinel-facies rocks which are at least as

much common as garnet-bearing ones. Furthermore, garnet peridotites always have some coexisting spinel, more and more enriched in the chromite end-member and in ever smaller amounts as pressure increases, to the exception of a very few of the deepest samples. Last, any of these rock types may also have small amounts of sulphides, ilmenite, phlogopite, etc.

Two phases clearly dominate all the assemblies in terms of modal composition: olivine and orthopyroxene. These phases may thus provide critical alternatives for the physical modeling of the mantle, inasmuch as they should be less prone to metasomatic perturbations. Indeed, under the low-stress steady-state conditions of the mantle, these dominant phases may grow to large sizes as illustrated by the uppermost harzburgites. On the other hand, in the case where metasomatic fluids would induce disequilibrium melting of crystals, olivine and orthopyroxene also have the highest melting points (e.g. over 120K difference between ortho- and clinopyroxene at 3GPa), which makes the structure more stable and reduces diffusion. However, the solid solutions buffered through transfer reactions are very limited in extent (e.g., commonly about 200 and 20 ppm for Ca and Al, respectively, in olivine, and 3000 ppm for either element species in orthopyroxene). Thermodynamic modeling must thus be very precise and high-quality composition data collected on specifically equipped microprobes.

Before developing such tools, it is necessary to check whether the two dominant phases, olivine and orthopyroxene, were indeed sufficiently preserved from metasomatism to be used in thermobarometry. This was done by quantitatively scanning selected domains or through traverses, both checking for eventual progressive compositional variations and for the existence of limited microdomains. Checks were performed on both sides of original grain boundaries as little opened as possible during late serpentinisation to ensure difference could be made between formerly "clean" grain-boundaries and those clearly marked by passing metasomatic fluids. As many mineral species couples as possible were studied, and shielded inclusion boundaries were investigated separately.

Evidence of significant peripheral metasomatism is observed in many samples, but the intensity of the perturbations on olivine and orthopyroxene could not be related to that of modal metasomatism

characterized by the occurrence of phlogopite or destabilization of phases such as spinel, garnet and/or clinopyroxene. For instance, foliated spinel lherzolites (IUGS-wise) collected at Letseng show no evidence of modal metasomatism and display steady-state textures (elongated grains 0,3x0,4 mm for all phases, spinel included) while their phase compositions vary within crystals and according to the nature of the nearest phases. In other samples, orthopyroxenes are locally overgrown usually over distance of 0,1 to 0,2 mm, with a clear discontinuity in composition (Table 1; Fig. 1)

Table 1: Orthopyroxene overgrowths*

	Cores	Overgrowths
Ti	0 - 6	119 - 156
Fe	1308 - 1348	1468 - 1663
Ca	77 - 90	418 - 436
Na	4 - 17	70 - 91

* Compositional brackets for orthopyroxene overgrowths relative to cores. Concentrations of the selected elements are given in site fractions x 10000. Sample THB-9801.
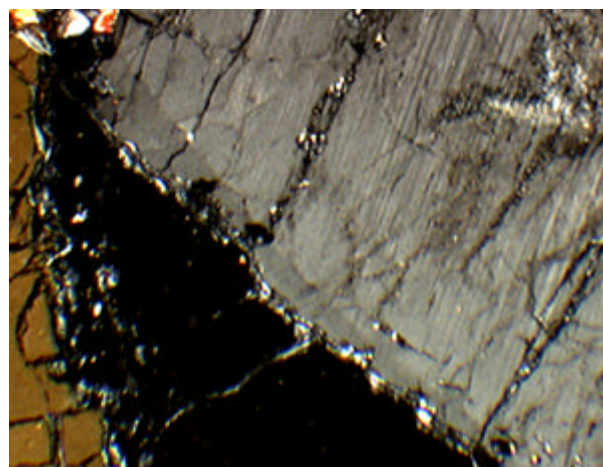

Figure 1. Overgrowth of orthopyroxene on an orthopyroxene core. Sample THB-9801. Scale = 1.85 mm across

However, with but only a very few exceptions, cores of olivines and orthopyroxenes are very homogeneous, with a clear correlation between concentrations in both phases for the major elements measured as traces on Cameca probes (Camparis, University Paris-VI, France) through a specific software (Fialin et al., 1999), with total counting times par element of 500 to 1000 s, at 30 kV and 500nA (SX-50). For examples, some olivine cores are homogeneous to less than 1 ppm (for Ti), and

orthopyroxene cores and rims to less than 5 ppm for Cr or 25 ppm for Al, which allows identification of rims despite minute differences in absolute concentrations equivalent to 6, 5 and 1%, respectively. Hence, routine automatic analyses of cores for elements such as Ca, Na, Al, Cr an Ti should yield concentrations significant enough to apply eventual thermobarometers experimentally calibrated.

INVERSION FOR OPX IN THE CMS SYSTEM

Pyroxene thermobarometry has become more and more sophisticated in the past decades with the conjunction of ever better experimental and analytical data for a larger panel of chemical systems, and of better-structured thermodynamic models calling upon more powerful data-processing mathematical tools. Still, constants in the theoretical equations are but fitting parameters to the equilibrium data and refer to fictive models which are an a priori choice of the operator. Moreover, better adjustment is sometimes achieved, even recently, through invalid modifications of the basic thermodynamic equations. With regard to such uncertainties, the parameters for limited solutions could thus not really be extracted from the experimental data. Contrastingly, general inversion is an objective and powerful way of data processing which reduces to virtually nil the prior assumptions and much better describes these data.

The orthopyroxene solvus provides a typical example of such results. By considering a set of transfer reactions (Mercier and Bertrand, 1984) written as En(cpx)⇔En(opx) and Di(opx)⇔Di(cpx), the sufficient condition for equilibrium is given by solving simultaneously the two equations

$$\mathbf{m}_{En}^{opx} = \mathbf{m}_{En}^{cpx} \text{ and } \mathbf{m}_{Di}^{opx} = \mathbf{m}_{Di}^{cpx}$$

where the chemical potential for each phase is

$$\mathbf{m}_i = U_i + V_i P - S_i T + RT\ln\Omega_i - X_i^2 W_{ij} + 2X_i X_j (W_{ij} - W_{ji})$$

where Ω_i is the configurational probability of the component i, and W, the Margules parameters such as

$$W = W_U + W_V P - W_S T$$

Following most workers since Lindsley and Dixon (1976), only strictly reversed overlapping data have been processed to limit the effects of possibly distinct reaction kinetics upon either exsolution or dissolution, which yields a dataset of 44 experiments for temperature and pressure conditions (listed in Coussaert et al., 2002) ranging from 896 to 1500°C and 0,2 to 6,0 GPa, respectively. Former modeling strategies included least-squares regressions of mid-bracket values (Lindsley et al., 1981), solving sets of linear inequalities derived from the thermodynamic functions and written in terms of the bracket end-values (Carlson and Lindsley, 1988) or in a Monte-Carlo-type trial-and-error adjustment of *a priori* thermodynamic parameters to the experimental dataset (Gasparik, 1990). However, the basic equations are non linear and the input data have to be hand-adjusted to get the models better fit the real experimental brackets, whether the equations are solved iteratively one at a time (Lindsley and Davidson, 1980) or through linear programming (Carlson, 1988) with corrections according to the operator's perception of misfits.

Furthermore, in either case, the form of the equations yields a strongly dominant role to the clinopyroxene composition (much larger variations) relative to that of orthopyroxene, even more when solving first for the En-reaction (perceived as more easily fitting the data) which is well known to be virtually insensitive to the orthopyroxene composition. (Bertrand and Mercier, 1985). Therefore, orthopyroxene solvi constructed from such thermobarometers cannot have a precision sufficient to be used to test for equilibrium between coexisting pyroxenes or to estimate P-T conditions from the only analyses of orthopyroxenes of natural rocks.

Contrastingly, general inversion (Tarantola and Valette, 1982) truly solves simultaneously for the two thermodynamic equations by directly processing the data set as a whole without meddling any of the values at any time. This mathematical procedure provides a least-squares fit of theoretical-law parameters to a dataset through probability density functions, by minimizing the error on the parameters with the constraints of prior errors on the data as well as on the parameters themselves. The posterior covariance matrix associated to the parameters makes each one of them known with a confidence interval which has a physical meaning. Furthermore, unlike the stepwise strategy used by Bertrand and others (1986), the approach to data

processing is now changed so the mathematical procedure becomes completely objective.

The most general form of the equation is first used to extract qualitative information upon the significance of each term and to *a posteriori* decide of which ones should be kept in the modeling process. This is illustrated (Figure 2) through inversion for simpler equations (eventual asymmetries of the Margules parameters has been discarded here).
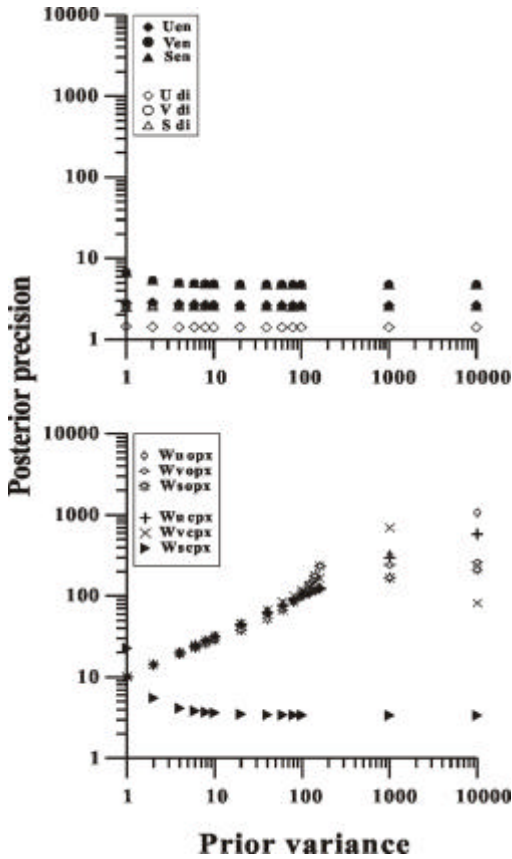

Figure 2 : Posterior precision (standard deviation / model value) as a function of a priori fixed variances for parameters describing equilibrium between two regular symmetric pyroxenes.

All end-member energy terms are clearly independent (constant precision) of the prior statistics imposed by the operator (variance), while all Margules parameters appear not to be constrained by the dataset (precision with erratic behavior or correlated to the variance), except for W_S which would be the only excess parameter kept for the final inversion. Through this powerful method, the final CMS equations also tested for asymmetry terms obey a symmetric orthopyroxene–asymmetric clinopyroxene model, still with W_S terms as the

only excess parameters. Accordingly, the equations read as follows:

for the enstatite-component reaction,

$$\Delta U^e + \Delta V^e P - \Delta S^e T =$$
$$-RT\ell n(X_{Mg}^{M2,cpx}/X_{Mg}^{M2,opx}) + (X_{Ca}^{M2,cpx})^2 W_S^{ce} T$$
$$-2(X_{Ca}^{M2,cpx})^2 X_{Mg}^{M2,cpx}(W_S^{ce} - W_S^{cd})T - (X_{Ca}^{M2,opx})^2 (W_S^o T)$$

or

$$27700 + 487P - 12{,}5T =$$
$$-RT\ell n(X_{Mg}^{M2,cpx}/X_{Mg}^{M2,opx}) - 13T(X_{Ca}^{M2,cpx})^2$$
$$+17{,}68T(X_{Ca}^{M2,cpx})^2 X_{Mg}^{M2,cpx} + 23{,}8T(X_{Ca}^{M2,opx})^2$$

and for the diopside-component reaction,

$$\Delta U^d + \Delta V^d P - \Delta S^d T =$$
$$-RT\ell n(X_{Ca}^{M2,opx}/X_{Ca}^{M2,cpx}) - (X_{Mg}^{M2,cpx})^2 W_S^{cd} T$$
$$+2(X_{Mg}^{M2,cpx})^2 X_{Ca}^{M2,cpx}(W_S^{cd} - W_S^{ce})T + (X_{Mg}^{M2,opx})^2 (W_S^o T)$$

or

$$41100 + 1660P - 28{,}6T =$$
$$-RT\ell n(X_{Ca}^{M2,opx}/X_{Ca}^{M2,cpx}) + 5{,}84T(X_{Mg}^{M2,cpx})^2$$
$$+17{,}68T(X_{Mg}^{M2,cpx})^2 X_{Ca}^{M2,cpx} - 23{,}8T(X_{Mg}^{M2,opx})^2$$

Application to the natural system implies taking into account all cations found in significant amounts on the various sites according to the solution model best suitable to each one. Again, general inversion yields small but significant differences relative to former models, for instance, with some reciprocal Al effect in orthopyroxene (formerly neglected), a better ternary approach to Na competition for M2 sites (substitution essentially for Ca) , etc.

CONCLUSION

Peridotite xenoliths from kimberlites have variable amounts of clinopyroxene which has always been affected by metasomatism, whether some such pyroxene already existed in the protolith or not. All mantle models based on the postulate that this phase belonged to an olivine-orthopyroxene-clinopyroxene-garnet equilibrium must thus be revisited. As olivine and orthopyroxene have generally retained the signature of the original equilibrium in their cores, precise thermodynamic models of their limited solid solutions based on available experimental data should provide tools to test how much former estimates could have been shifted by metasomatism relative to real mantle conditions. General inversion applied to the available experimental datasets proves

that a substantial revision of the theoretical form of thermodynamic equations is mandatory to reach the precision required for such an application, but the present work on thermobarometers and natural phase chemistry shows this goal to be at close reach.
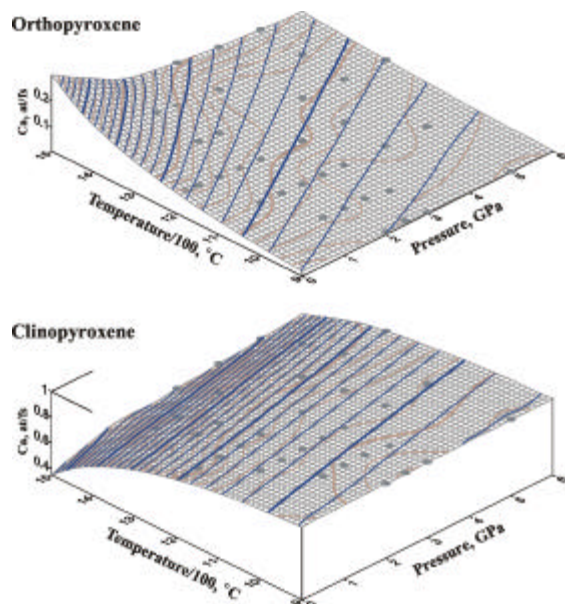

Figure 4: Solvi for the final symmetric orthopyroxene – asymmetric clinopyroxene model (isopleths in blue), shown together with the experimental data points and solvi-like free-surface isopleths obtained under Surfer® software for strict adherence to the data.

REFERENCES

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 Sc Lett 76: 109-122

Bertrand, P., Sotin C., Mercier, J-C.C., Takahashi, E., 1986 From the simplest chemical system to the natural one: garnet peridotite barometry. Contrib Mineral Petrol 93: 168-178

Boyd, F.R., 1973. A pyroxene geotherm. Geochim Cosmochim Acta 37, 2533-2546

Boyd, F.R., Pearson, D.G., Nixon, P.H., Mertzman, S.A., 1993. Low-calcium garnet harzburgites from southern Africa: their relations to craton structure and diamond crystallization. Contrib. Mineral. Petrol. 113, 352-366.

Carlson, W.D., 1988 Subsolidus phase equilibria on the forsterite-saturated join $Mg_2Si_2O_6$-$CaMgSi_2O_6$ at atmospheric pressure. Am Mineral 73: 232-241

Carlson, W.D., Lindsley, D.H. (1988) Thermochemistry of pyroxenes on the join $Mg_2Si_2O_6$-$CaMgSi_2O_6$. Am Mineral 73, 242-252

Coussaert, N., Mercier, J-C.C., Demaiffe, D., André, L., 2002. Formal modeling of the CaO-MgO-SiO_2 orthopyroxene-clinopyroxene binary through general inversion. Contrib Mineral Petrol (soumis).

Fialin, M., Rémy, H., Richard, C., Wagner, C., 1999. Trace element analysis with the electron microprobe: new data ans perspectives. Am Mineral 84, 70-77.

Gasparik, T., 1990. A thermodynamic model for the enstatite-diopside join. Am Min 75: 1080-1091

Lindsley, D.H., Davidson, P.M., 1980. Discussion of thermodynamic parameters of $Mg_2Si_2O_6$-$CaMgSi_2O_6$ pyroxenes based on regular solution and cooperative disordering models. Contrib Mineral Petrol 75: 301-304

Lindsley, D.H., Dixon, S.A., 1976. Diopside-enstatite equilibria at 850°C to 1400°C, 5 to 35 kbar. Am J Sci 276:1285-1301

Lindsley, D.H., Grover, J.E., Davidson, P.M., 1981. The thermodynamics of the $Mg_2Si_2O_6$-$CaMgSi_2O_6$ join: a review and an improved model. Adv Phys Geochem 1:179-175

Mercier, J-C.C., Bertrand, P., 1984. Thermobarométrie pyroxénique: quelques méthodes basées sur des réactions de transfert. In Thermométrie et barométrie géologiques, Soc Fr Mineral Cristallogr, Paris, 1, 237-280

Streckeisen, A.L., 1973. Plutonic rocks: classification and nomenclature recommended by the I.U.G.S. subcommission on the systemaztics of igneous rocks. Geotimes 18, 26-30

Tarantola, A., Valette, B., 1982. Generalized non-linear inverse problems solved using the least-square criterion. Rev Geophys Space Phys 2: 219-232

Wood, B., Banno, S., 1973. Garnet-orthopyroxene and orthopyroxene–clinopyroxene relationship in simple and complex systems. Contrib Mineral Petrol 42, 109-124

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