Thermometric effect of measured vs. estimated Fe^{3+}/Fe_{tot} in minerals from granulites

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Scope of research

Physical and chemical processes in the lithospheric shell of the Earth can be unravelled by studying metamorphic rocks that were deeply buried during collision events of continental plates and have then returned to the surface. Such rocks offer insights into depths not accessible by any other direct means. The understanding of processes in the lithosphere depends on whether information recorded in exhumed high-pressure rocks can be reliably retrieved. Much current debate surrounds the peak temperatures achieved during high-pressure metamorphism of granulites. For such rocks, peak-temperature estimates above 1000 °C have been inferred from feldspar thermometry and garnet-clinopyroxene Fe^{2+}-Mg exchange thermometry (e.g., [1]). However, ternary feldspars that undoubtedly indicate ultrahigh-temperature conditions have been reinterpreted as mineral relics inherited from the magmatic precursors of the rocks, whereas identical temperature estimates obtained using garnet-clinopyroxene thermometry have been questioned as equilibrium conditions because of the continuation of Fe^{2+}-Mg diffusion at lower temperatures ([2]). The different temperature estimates translate into contrasting evolution paths for the rocks, all the more because pressure estimates made from barometric mineral reactions change with temperature. Apart from effects of post-peak diffusion, the garnet-clinopyroxene Fe^{2+}-Mg exchange thermometry is fraught with uncertainty arising from a usual lack of measured Fe^{3+}/Fe_{tot} ratios in both minerals ([3]). We have solved this problem by micro-XANES analysis. However, knowing the Fe^{3+}/Fe_{tot} ratios in minerals does not solve all difficulties with Fe^{2+}-Mg exchange thermometry, because experimental calibrations of Fe^{2+}-Mg exchange reactions were based mostly on highly reduced compositions. Therefore, applying such calibrations to chemical systems that involve an Fe_2O_3 component causes uncertainty, even if the Fe^{3+} content in the minerals is known. Calibrating the temperature dependence of Fe^{2+}-Mg exchange reactions in Fe_2O_3-bearing chemical systems thus remains a challenging problem.

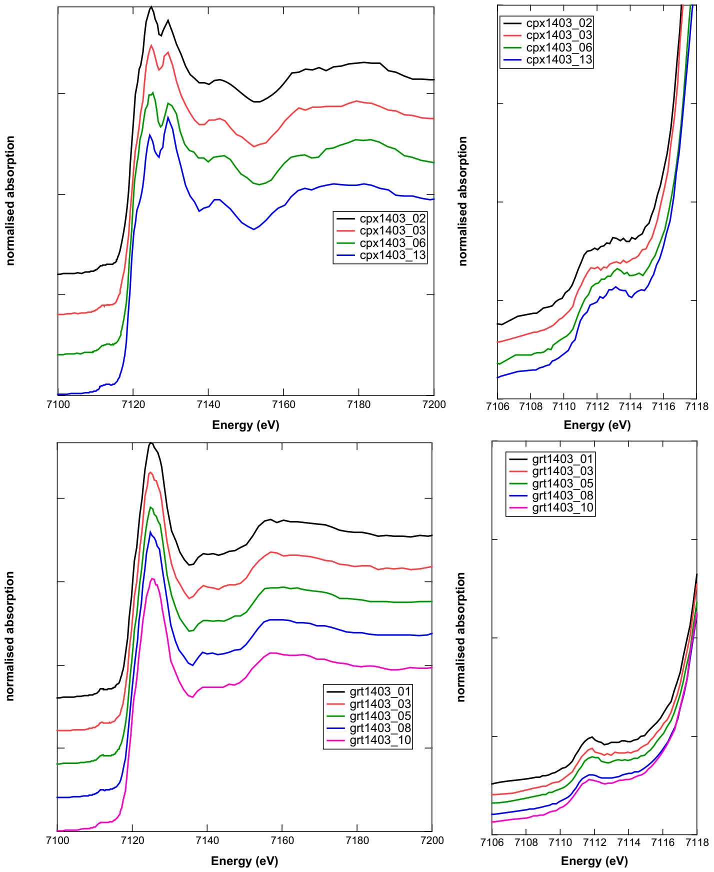

Fig. 1: (top left) XANES spectra of clinopyroxene from sample 1403. (top right) Zoom of pre-edge region. (bottom left) XANES spectra of garnet from sample 1403. (bottom right) Zoom of pre-edge region.

Operating conditions

The experiments were run at earlier described operating conditions ([3]).

Sample description

Among the investigated high-pressure rocks, we focus here on a mafic granulite interlayered in garnet peridotite from the Saxon Granulite Massif. The garnet peridotite is thought to be derived from extremely high depths (>400 km) in the transition zone of the Earth's mantle. This interpretation has been favoured over an equally possible origin in the upper Earth's mantle ([4]). The mantle rocks have recrystallized at P-T conditions of ca. 2.5 GPa and 1000-1030 °C ([4]), i.e. close to the peak P-T stage in the enveloping granulites estimated at 2.2-2.3 GPa and >1000 °C ([1]). The imbrication of the mantle rocks between deeply buried continental crust rocks may thus have occurred under these conditions. The studied quartz-free mafic granulite consists mainly of garnet and clinopyroxene. Clinopyroxene, plagioclase, rutile and pyrite are found as inclusions in garnet. The early mineral assemblage is overgrown by amphibole, plagioclase and ilmenite. Temperature estimates calculated from the Fe^{2+}-Mg fractionation between core compositions of garnet and clinopyroxene, assuming a pressure of 2.2 GPa, are in the range of 990-1060 °C, with an average of 1032 ± 22 °C (1σ). Since the pyrite inclusions in garnet suggest a low oxidation state, the estimates were made from all-ferrous mineral formulae. Oxygen-isotope thermometry based on garnet-whole rock fractionation has yielded a temperature estimate of 1005 ± 23 °C ([5]), thus providing an independent confirmation of the ultrahigh-temperature conditions.

Results

The micro-XANES analysis of the Fe^{3+}/Fe_{tot} ratio in garnet and clinopyroxene has proved to be an effective means to increase the certainty of the Fe^{2+}-Mg exchange thermometry. The results can be used to decide wether the all-ferrous approach or stoichiometric estimation of Fe^{2+} leads to more realistic temperature estimates for the studied sample. This is important because the better suited approach discernable from a few micro-XANES data can be applied to more systematically collected electron-probe data. The measured Fe^{3+}/Fe_{tot} ratios in garnet are low (ranging from 0.01 to 0.06) and do not differ from stoichiometric estimates of this ratio. Clinopyroxene is higher in Fe^{3+}/Fe_{tot} than garnet and shows a clear difference between measured (0.09-0.24) and estimated (0.27-0.44) Fe^{3+}/Fe_{tot} ratios. As a result, X_{Mg} [$Mg/(Mg+Fe^{2+})$] in garnet does not change, regardless of whether the Fe^{3+} content is measured or estimated. In contrast, X_{Mg} in clinopyroxene varies strongly depending on whether the Fe^{3+} content is measured, estimated from stoichiometry or neglected. As exemplified for one pair of mineral compositions (Table 1), the differences in X_{Mg} of clinopyroxene have a strong effect on the garnet-clinopyroxene Fe^{2+}-Mg exchange thermometry. The temperature estimates are highest when total Fe in clinopyroxene is taken as all-ferrous, and lowest when Fe^{2+} in clinopyroxene is estimated by assuming ideal stoichiometry. Temperature estimates intermediate between these results were obtained using the Fe^{3+}/Fe_{tot} ratio calculated from micro-XANES data, with a difference of about 90 °C from the all-ferrous approach, and of about 150 °C when Fe^{2+} is estimated from stoichiometry. The micro-XANES-based garnet-clinopyroxene temperature estimate of 995 °C calculated at an assumed pressure of 2.2 GPa agrees well with a garnet-whole rock oxygen-isotope temperature of about 1005 °C analysed from the same rock.

Table 1. Garnet-clinopyroxene temperature estimates.

Sample	Garnet						Clinopyroxene			lnKd	T (°C) at P =	
	No.	XPrp	XAlm	XGrs	XFe^{3+}	XMg	No.	XFe^{3+}	XMg		2.0 GPa	2.2 GPa
	all-ferrous mineral formulae											
1403	10	0.40	0.38	0.21	0.00	0.51	06	0.00	0.69	0.78	1083	1087
	XFe^{3+} calculated from micro-XANES data											
1403	10	0.40	0.38	0.21	0.01	0.51	06	0.24	0.75	1.05	990	995
	XFe^{3+} estimated from stoichiometry											
1403	10	0.40	0.38	0.21	0.01	0.51	06	0.44	0.80	1.32	836	841

Calculated using the calibration from [6]; $XFe^{3+} = Fe^{3+}/Fe_{tot}$.

References

[1] Rötzler, J., Romer, R. L., Budzinski, H., Oberhänsli, R. Europ. Jour. Mineral., 16, 917-937 (2004)

[2] Štípská, P. & Powell, R. Jour. Metamorphic Geol., 23, 627-647 (2005)

[3] Rötzler, J. & Wilke, M. HASYLAB Annual Report, Part I, 1109-1110 (2005)

[4] Massonne, H.-J. & Bautsch, H.-J. Intern. Geol. Rev., 44, 779-796 (2002)

[5] Hagen, B. Unpubl. Doctoral Thesis, University of Bonn, 169 p. (2002)

[6] Berman, R. G., Aranovich, L. Y., Pattison, D. R. M. Contrib. Mineral. Petrol., 119, 30-42 (1995)