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References

Barnes, S.-J., Naldrett, A.J. and Gorton, M.P. (1985). The origin of the fractionation of platinum-group elements in terrestrial magmas. *Chemical Geology*, **53**, 303-323.

Barnes, S.-J., Makovicky, E., Karup-Møller, S., Makovicky, M. and Rose-Hansen, J. (1994). Partition coefficients for Ni, Cu, Pd, Pt, Rh and Ir between monosulphide solid solution and sulphide liquid and the implications for the formation of compositionally zoned Ni-Cu sulphide bodies by fractional crystallisation of sulphide liquid. *Mineralogical Magazine*, **58A**, 51-52.

Barnes, S.-J., Makovicky, E., Makovicky, M., Rose-Hansen, J. and Karup-Møller, S. (1997). Partition coefficients for Ni, Cu, Pd, Pt, Rh and Ir between monosulfide solid solution and sulfide liquid and the formation of compositionally zoned Ni-Cu sulfide bodies by fractional crystallisation of sulfide liquid. *Canadian Journal of Earth Sciences*, **34**, 366-374.

Blum, J.D., Wasserburg, G.J., Hutcheon, I.D., Beckett, J.R. and Stolper, E.M. (1989). Diffusion, phase equilibria and partitioning experiments in the Ni-Fe-Ru system. *Geochimica et Cosmochimica Acta*, **53**, 483-489.

Bruwer, J.S. (1996). *Experimental investigation of the system Cu-Ni-S in the temperature interval 1200°C to 700°C*. M.Sc. thesis (unpublished), University of Pretoria, South Africa, 157pp.

Bryukvin, V.A., Shekhter, L.N., Reznichenko, V.A., Kuvinov, V.E., Blokhina, L.I. and Kukoyev, V.A. (1985). Phase equilibria in the system Fe-Pd-S. *Izvest. Akad. Nauk SSSR, Metally*, **4**, 25-28. (in Russian)

Burylev, B.P., Mechev, V.V., Tsemekhan, L.Sh., Romanov, V.D. and Vaisburd, S.E. (1974). Distribution of palladium and platinum between the metal and sulphide in Cu-S and Cu-Ni-S melts. *Izvest. Akad. Nauk SSSR, Metally*, 82-86. (in Russian)

Cabri, L.J. (1988). Application of proton and nuclear microprobes in ore deposit mineralogy and metallurgy. *Nuclear Instruments and Methods in Physics Research B*, **30**, 459-465.

Cabri, L.J. and Campbell, J.L. (1998). The proton microprobe in ore mineralogy (Micro-PIXE technique). *In: Modern Approaches to Ore and Environmental Mineralogy*. Ed: Cabri, L.J. and Vaughan, D.J. Mineralogical Association of Canada, Short Course Series, 27, Chapter 7, 181-198.

Cabri, L.J., Harris, D.C. and Nobiling, R. (1984a). Trace silver analyses by proton microprobe in ore evaluation. *In: Precious metals: Mining, extraction and processing*, Ed: Kudryk, V., Corrigan, D.A. and Liang, W.W. The Metallurgical Society of AIME, New York, 93-100.

Cabri, L.J., Blank, H., El Goresy, A., Laflamme, J.H.G., Nobiling, R., Sizgoric, M.B. and Traxel, K. (1984b). Quantitative trace-element analyses of sulphides from Sudbury and Stillwater by proton microprobe. *Canadian Mineralogist*, **22**, 521-542.

Campbell, J.L., Maxwell, J.A., Teesdale, W.J. and Wang, J.-X. (1990). Micro-PIXE as a compliment to electron probe microanalysis in mineralogy. *Nuclear Instruments and Methods in Physics Research B*, **44**, 347-356.

Campbell, J.L., Teesdale, W.J., Kjarsgaard, B.A. and Cabri, L.J. (1996). Micro-PIXE analysis of silicate reference standards for trace Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo and Pb, with emphasis on Ni for application of the Ni-in-garnet geothermometer. *Canadian Mineralogist*, **34**, 37-48.

Cemic, L. and Kleppa, O.J. (1986). High temperature calorimetry of sulphide systems. I. Thermochemistry of liquid and solid phases of Ni + S. *Geochimica et Cosmochimica Acta*, **50**, 1633-1641.

Chabot, N.L. and Drake, M.J. (1997). An experimental study of silver and palladium partitioning between solid and liquid metal, with applications to iron meteorites. *Meteoritics and Planetary Science*, **32**, 637-645.

Chakrabarti, D.J. and Laughlin, D.E. (1986). Cu-S. *In: Binary Alloy Phase diagrams*, Volume 1, Massalski, T.B. (Editor). American Society for Metals, Ohio, 953-957.

Chuang, Y. –Y, Hsieh, K.-C., and Austin Chang, Y. (1985). Thermodynamics and phase relationships of transition metal-sulfur systems: Part V. A re-evaluation of the Fe-S system using an associated solution model for the liquid phase. *Metallurgical Transactions*, **16B**, 277-285.

Cousens, D.R., French, D.H., Ramsden, A.R., Griffin, W.L., Ryan, C.G. and Sie, S.H. (1989). Application of the proton microprobe to the partitioning of Platinum Group Elements in sulphide and oxide phases. *Mineralogy-Petrology Symposium*, Sydney NSW, 45-49.

Crocket, J.H., Fleet, M.E. and Stone, W.E. (1997). Implications of composition for experimental partitioning of platinum-group elements and gold between sulfide liquid and basalt melt: The significance of nickel content. *Geochimica et Cosmochimica Acta*, **61**, 4139-4149.

Czamanske, G.K., Kunilov, V.E., Zientek, M.L., Cabri, L.J., Likhachev, A.P., Calk, L.C. and Oscarson, R.L. (1992). A proton-microprobe study of magmatic sulfide ores from the Noril'sk-Talnakh district, Siberia. *Canadian Mineralogist*, **30**, 249-287.

Czamanske, G.K., Sisson, T.W., Campbell, J.L. and Teesdale, W.J. (1993). Micro-PIXE analysis of silicate reference standards. *American Mineralogist*, **78**, 893-903.

Distler, V.V. (1980). Solid solutions of platinoids in sulphides. *In: Sulphosalts, platinum minerals and ore microscopy*. Proceedings of the General Meeting IMA, Novosibirsk 1978. IGEM Akad. Nauk SSSR, Nauka, 191-200. (in Russian)

Distler, V.V., Malevskiy, A. Yu. and Laputina, I.P. (1977). Distribution of platinoids between pyrrhotite and pentlandite in crystallisation of a sulphide melt. *Geochemistry International*, **14**, 30-40.

Fleet, M.E. (1987). Structure of godlevskite, Ni_9S_8. *Acta Crystallography*, **C43**, 2255-2257.

Fleet, M.E. (1988). Stoichiometry, structure and twinning of godlevskite and synthetic low-temperature Ni-excess nickel sulphide. *Canadian Mineralogist*, **26**, 283-291.

Fleet, M.E. and Stone, W.E. (1991). Partitioning of platinum-group elements in the Fe-Ni-S system and their fractionation in nature. *Geochimica et Cosmochimica Acta*, **55**, 245-253.

Fleet, M.E., Chryssoulis, S.L., Stone, W.E. and Weisener, C.G. (1993). Partitioning of platinum-group elements and Au in the Fe-Ni-Cu-S system: experiments on the

fractional crystallisation of sulphide melt. *Contributions to Mineralogy and Petrology*, **115**, 36-44.

Fleet, M.E., Liu, M and Crocket, J.H. (1999). Partitioning of trace amounts of highly siderophile elements in the Fe-Ni-S system and their fractionation in nature. *Geochimica et Cosmochimica Acta*, **63**, 2611-2622.

Franklyn, C.B. and Merkle, R.K.W. (1999). Milli-PIXE of co-existing cooperite and braggite - a comparison with electron microprobe analysis. *Nuclear Instruments and Methods in Physics Research B*, **158**, 550-555.

Franklyn, C.B. and Merkle, R.K.W. (2001) Surface contamination by smearing during polishing – a PIXE study. *Nuclear Instruments and Methods in Physics Research B*, **181**, 140-144.

Franklyn, C.B., Ueckermann, H. and Merkle, R.K.W. (2001) Accidental surface contamination – the effect on trace element analysis. *Nuclear Instruments and Methods in Physics Research B*, **181**, 145-149.

Gerlach, von J., Hennig, U. and Park, H.S. (1972). Über die Edelmetallverteilung auf Stein und Speise. *Erzmetall*, **25**, 69-77.

Gueddari, K., Piboule, M. and Amosse, J. (1996). Differentiation of platinum-group elements (PGE). and of gold during partial melting of peridotites in the lherzolitic massifs of the Betico-Rifean Range (Ronda and Beni Bousera). *Chemical Geology*, **134**, 181-197.

Halden, N.M., Campbell, J.L. and Teesdale, W.J. (1995). PIXE analysis in mineralogy and geochemistry. *Canadian Mineralogist*, **33**, 293-302.

Johansson, S.A.E. (1992). Particle Induced X-ray Emission and Complementary Nuclear Methods for trace element determination. *Analyst*, **117**, 259-265.

Jones, J.H. and Drake, M.J. (1983). Experimental investigations of trace element fractionation in iron meteorites, II: The influence of sulfur. *Geochimica et Cosmochimica Acta*, **47**, 1199-1209.

Jones, J.H. and Drake, M.J. (1986). Geochemical constraints on core formation in the earth. *Nature*, **322**, 221-228.

Jones, J.H. and Malvin, D.J. (1990). A non metal interaction model for the segregation of trace metals during solidification of Fe-Ni-S, Fe-Ni-P, and Fe-Ni-S-P alloys. *Metallurgical Transactions*, **21B**, 697-706.

Jones, J.H., Benjamin, T.M., Maggiore, C.M., Duffy, C.J. and Hart, S.R. (1986). Experimental partitioning of Ag, Mo, Pb and Pd between iron metal and troilite. *Proceedings of the 17th Lunar Planetary Science Conference*, 400-401.

Karup-Møller, S. and Makovicky, E. (1993). The system Pd-Ni-S at 900°, 725°, 550° and 400°C. *Economic Geology*, **88**, 1261-1268.

Karup-Møller, S. and Makovicky, E. (1999). The phase system Cu-Pd-S at 900°C, 725°C, 550°C and 400°C. *Neues Jahrbuch fur Mineralogie, Monatshefte*, 551-567.

Kolonin, G.R., Peregoedova, A.V. and Sinyakova, E.F. (1997). The physical-chemical model of fractionation of Pt, Ir and light PGE during crystallisation of sulphide melts. *The Betekhtin Symposium* (Moscow), Abstracts 270-271. (in Russian)

Kulagov, E.A., Evstigneeva, T.L. and Yushko-Zakharova, O.E. (1969). The new nickel sulphide, godlevskite. *Geol. Rudnykh. Mestorozhderii*, **11**, 115-121. (in Russian)

Kullerud, G. (1960). The Cu-S system. *Carnegie Institution of Washington Year Book*, **59**, 110-111.

Kullerud, G. (1961). Two-liquid field in the Fe-S system. *Carnegie Institution of Washington Year Book*, **60**, 174-176.

Kullerud, G. (1971). Experimental techniques in dry sulphide research. *In: Research techniques for high pressure and high temperatures.* Editor: G.C. Ulmer, Springer-Verlag, Berlin Heidelberg New York, 289-315.

Kullerud, G. and Yoder, H.S. (1959). Pyrite stability relations in the Fe-S system. *Economic Geology*, **54**, 533-572.

Kullerud, G. and Yund R.A. (1962). The Ni-S system and related minerals. *Journal of Petrology*, **3**, 126-175.

Legendre, O. and Auge, T. (1986). Mineralogy of platinum-group mineral inclusions in chromitites from different ophiolitic complexes. *In: Metallogeny of basic and ultrabasic rocks*. Editors: M.J. Gallagher *et al.*, Institute of Mining and Metallurgy, 361-372.

Li, C. and Barnes, S.-J. (1996). Partitioning of platinum-group elements and Au in the Fe-Ni-Cu-S system: experiments on the fractional crystallisation of sulphide melt – a discussion. *Contributions to Mineralogy and Petrology*, **123**, 435-437.

Li, C., Barnes, S.-J., Makovicky, E., Rose-Hansen, J.R. and Makovicky, M. (1996). Partitioning of Ni, Cu, Ir, Rh, Pt and Pd between monosulfide solid solution and sulfide liquid: effects on composition and temperature. *Geochimica et Cosmochimica Acta*, **60**, 1231-1238.

Lin, R.Y., Hu, D.C. and Chang, Y.A. (1978). Thermodynamics and phase relations of transition metal - sulfur systems. II. The nickel-sulfur system. *Metallurgical Transactions*, **9B**, 531-538.

Makovicky, E. and Karup-Møller, S. (1993). The system Pd-Fe-S at 900°, 725°, 550° and 400°C. *Economic Geology*, **88**, 1269-1278.

Makovicky, E. and Karup-Møller, S. (1994). The phase system Cu-Rh-S at 900°C, 725°C and 500°C. *7th International Platinum Symposium* (Moscow, Russia), Abstracts, 70-71.

Makovicky, E. and Karup-Møller, S. (1995). The system Pd-Fe-Ni-S at 900 and 725°C. *Mineralogical Magazine*, **59**, 685-702.

Makovicky, M., Makovicky, E. and Rose-Hansen, J. (1986). Experimental studies on the solubility and distribution of platinum group elements in base-metal sulphides in platinum deposits. *In: Metallogeny of basic and ultrabasic rocks*. Editors: M.J. Gallagher *et al.*, Institute of Mining and Metallurgy, 415-425.

Makovicky, M., Makovicky, E. and Rose-Hansen, J. (1988). Experimental evidence of the formation and mineralogy of platinum and palladium ore deposits. *In: Mineral Deposits within the European Community.* Editors: J. Boissonnas and P. Omenetto. Berlin-Heidelberg, Springer-Verlag, 303-317.

Makovicky, E., Karup-Møller, S., Makovicky, M. and Rose-Hansen, J. (1990). Experimental studies on the phase systems Fe-Ni-Pd-S and Fe-Pt-Pd-As-S applied to PGE deposits. *Mineralogy and Petrology*, **42**, 307-319.

Maxwell, J.A., Campbell, J.L. and Teesdale, W.J. (1989). The Guelph PIXE software package. *Nuclear Instruments and Methods in Physics Research B*, **43**, 218-230.

Maxwell, J.A., Teesdale, W.J. and Campbell, J.L. (1994). Compensation schemes for peak-tailing uncertainties in PIXE spectra, using the GUPIX code. *Nuclear Instruments and Methods in Physics Research B*, **94**, 172-179.

Maxwell, J.A., Teesdale, W.J. and Campbell, J.L (1995). The Guelph PIXE software package II. *Nuclear Instruments and Methods in Physics Research B*, **95**, 407-421.

Merkle, R.K.W. and Franklyn, C.B. (1999). Milli-PIXE determination of trace elements in osmium-rich platinum-group minerals from the Witwatersrand basin, South Africa. *Nuclear Instruments and Methods in Physics Research B*, **158**, 556-561.

Merkle, R.K.W., Franklyn, C.B., Przybylowicz, W. and Verryn, S.M.C. (in print). Submitted to *Nuclear Instruments and Methods in Physics Research B.*

Morimoto, N. and Gyobu, A. (1971). The composition and stability of digenite. *American Mineralogist*, **56**, 1889-1909.

Naldrett, A.J. (1981). Nickel sulphide deposits: Classification, composition, and genesis. *Economic Geology 75th Anniversary Volume*, 628-685.

Naldrett, A.J. (1989). Magmatic sulphide deposits. *Oxford Monographs on Geology and Geophysics*, Number 14, Clarendon Press, New York.

Naldrett, A.J., Gasparrini, E., Buchan, R. and Muir, J.E. (1972). Godlevskite (β-Ni_7S_6). from the Texmont mine, Ontario. *Canadian Mineralogist*, **11**, 879-885.

Naldrett, A.J., Hoffman, E.L., Green, A.H., Chou, C.-L. and Naldrett, S.R. (1979). The composition of Ni-sulfide ores, with particular reference to their content of PGE and Au. *Canadian Mineralogist*, **17**, 403-415.

Naldrett, A.J., Innes, D.G., Sowa, J. and Gorton, M.P. (1982). Compositional variations within and between five Sudbury ore deposits. *Economic Geology*, **77**, 1519-1534.

Noddack, Von W, Noddack, I. and Bohnstedt, U. (1940). Die Teilungskoeffizienten der Schwermetalle zwischen Eisensulfid und Eisen. I. *Zeitschrift für Anorganische und Allgemeine Chemie*, **244**, 252-280.

Page, N.J. and Talkington, R.W. (1984). Palladium, platinum, rhodium, ruthenium and iridium in peridotites and chromitites from ophiolite complexes in Newfoundland. *Canadian Mineralogist*, **22**, 137-149.

Paktunc, A.D., Hulbert, L.J. and Harris, D.C. (1990). Partitioning of the platinum-group and other trace elements in sulfides from the Bushveld Complex and Canadian occurrences of nickel-copper sulfides. *Canadian Mineralogist*, **28**, 475-488.

Palme, H. and Wlotzka, F. (1976). A metal particle from a Ca, Al-rich inclusion from the meteorite Allende, and the condensation of refractory siderophile elements. *Earth and Planetary Science Letters*, **33**, 45-60.

Pattou, L., Lorand, J.P. and Gros, M. (1996). Non-chondritic platinum-group element ratios in the earth's mantle. *Nature*, **379**, 712-715.

Peregoedova, A. (1997). The experimental study of Pt and Pd behaviour during crystallisation of Fe-Cu-Ni sulphide melts. *European Journal of Geosciences Conference 9*, Abstract 58/5P11.

Remond, G., Cesbron, F., Traxel, K., Campbell, J.L. and Cabri, L.J. (1987). Electron Microprobe analysis and Proton Induced X-ray Spectrometry applied to trace

element analysis in sulfides: problems and prospects. *Scanning Microscopy*, **1**, 1017-1037.

Rogers, P.S.Z., Duffy, C.J. and Benjamin, T.M. (1987). Accuracy of standardless nuclear microprobe trace element analyses. *Nuclear Instruments and Methods in Physics Research B*, **22**, 133-137.

Romanov, V.D., Mechev, V.V., Vaisburd, S.E. and Tsemekhan, L.Sh. (1973). Iridium, ruthenium and osmium in systems Cu-Cu_2S and Cu-Cu_2O. *Soviet Journal of Non-Ferrous Metals*, **14**, 13-14.

Rudashevskiy, N.S., Mochalov, A.G., Shkursky, V.V., Shumskaya, N.I. and Men'shikov, Y.P. (1984). The first discovery of malanite $Cu(Pt,Ir,Rh)_2S_4$ in the USSR. *Mineralogicheskiy Zhurnal*, **6**, 93-97. (in Russian with English abstract)

Rudashevskiy, N.S., Menachikov, Y.N., Mochalov, A.G., Trubkin, N.V., Shumskaya, N.I. and Zhdanov, V.V. (1985). Cuprorhodsite $CuRh_2S_4$ and cuproiridsite $CuIr_2S_4$, new natural thiospinels of platinum-group elements. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva*, **114**, 187-195. (in Russian)

Ryan, C.G., Cousens, D.R., Sie, S.H., Griffin, W.L. and Suter, G.F. (1990). Quantitative PIXE microanalysis of geological material using the CSIRO proton microprobe. *Nuclear Instruments and Methods in Physics Research B*, **47**, 55-71.

Schlitt, W.J. and Richards, K.J. (1973). The behaviour of selenium and tellurium in metal-matte systems. *Metallurgical Transactions*, **4**, 819-825.

Schlitt, W.J. and Richards, K.J. (1975). The distribution of silver, gold, platinum and palladium in metal-matte systems. *Metallurgical Transactions*, **6B**, 237-243.

Schmitt, W., Palme, H., and Wänke, H. (1989). Experimental determination of metal/silicate partition coefficients for P, Co, Ni, Cu, Ga, Ge, Mo, and W and some implication for the early evolution of the earth. *Geochimica et Cosmochimica Acta*, **53**, 173-185.

Sharma, R.C. and Chang, Y.A. (1980). Thermodynamics and phase relationships of transition metal-sulfur systems: IV. Thermodynamic properties of the Ni-S liquid phase and the calculation of the Ni-S phase diagram. *Metallurgical Transactions*, **11B**, 139-146.

Sie, S.H., Ryan, C.G., Cousens, D.R. and Griffin, W.L. (1989a). A Proton Microprobe for the Geosciences. *In: Ward, C.R. (Editor), Minpet 89: Mineralogy-Petrology Symposium.* Australasian Institute of Mining and Metallurgy, Sydney, 7-10.

Sie, S.H., Ryan, C.G., Suter, G.F., Cousens, D.R. and Griffin, W.L. (1989b). Determination of noble metals at crustal abundances. *In: Ward, C.R. (Editor), Minpet 89: Mineralogy-Petrology Symposium.* Australasian Institute of Mining and Metallurgy, Sydney, 33-35.

Simon, J.L. (1997). *Resampling: The "New Statistics"*. 2nd edition. Resampling Stats Inc. Arlington, VA, 436pp.

Skinner, B.J., Luce, F.D., Dill, J.A., Ellis, D.E., Hagen, H.A., Lewis, D.M., Odell, D.A., Sverjensky, D.A. and Williams, N. (1976). Phase relations in ternary portions of the system Pt-Pd-Fe-As-S. *Economic Geology*, **71**, 1469-1475.

Stone, W.E., Crocket, J.H. and Fleet, M.E. (1990). Partitioning of palladium, iridium, platinum and gold between sulphide liquid and basalt melt at 1200°C. *Geochimica et Cosmochimica Acta*, **54**, 2341-2344.

Taylor, J.R. (1983). A thermodynamic study of the distribution of metals between copper matte and bullion. *Advances in sulfide smelting*, 1, TMS-AIME, New York, 217-229.

Urban, H., Zereini, F., Skerstupp, B. and Tarkian, M. (1995). The determination of platinum-group elements (PGE). by nickel sulfide fire-assay: Coexisting PGE-phases in the nickel sulfide button. *Fresenius' Journal of Analytical Chemistry*, **352**, 537-543.

Walker, R.J., Hanski, E., Vuollo, J., and Liipo, J. (1996). The Os isotopic composition of Proterozoic upper mantle: evidence for chondritic upper mantle from the Outokumpu ophiolite, Finland. *Earth and Planetary Science Letters*, **141**, 161-173.

Willis, J. and Goldstein, J.I. (1982). The effects of C, P and S on trace element partitioning during solidification in Fe-Ni alloys. *Proceedings of the 13th Lunar Planetary Science Conference Part 1: Journal of Geophysical Research 87*, Supplement, A435-A445.

Appendix: Tables of experimental compositions and conditions.

Table A1. Ni-S charges for the 1200°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction		Melt		1200°C	Remarks
	Ni	S	Pt	Pd	Rh	Ni	S	Pt	Pd	Rh		°C	Days	°C	Days	Days	
136	1.6974	0.2996	0.0012	0.0010	0.0010	84.862	14.979	0.060	0.050	0.050		800	13			9	Separated, resealed
																2	Separated
142	0.4225	0.0746	0.0010	0.0010	0.0010	84.483	14.917	0.200	0.200	0.200	HU446	800	13			9	
143	0.4245	0.0740	0.0010			84.985	14.815	0.200	0.000	0.000	HU447	800	13			9	
144	0.4241	0.0749		0.0011		84.803	14.977	0.000	0.220	0.000	HU448	800	13			9	
145	0.4241	0.0750			0.0011	84.786	14.994	0.000	0.000	0.220	HU449	800	13			9	
146	0.8475	0.1499	0.0010	0.0010	0.0010	84.716	14.984	0.100	0.100	0.100	HU824	800	13			9	Separated, resealed
																2	

Table A2. Ni-S charges for the 1100°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction		Melt		1100°C	Remarks
	Ni	S	Pt	Pd	Rh	Ni	S	Pt	Pd	Rh		°C	Days	°C	Days	Days	
124	1.6974	0.2996	0.0010	0.0011	0.0010	84.866	14.979	0.050	0.055	0.050		800	47			13	Separated, resealed.
												800	4			13	Cracked in furnace, oxidised.
125	0.8479	0.1500	0.0011	0.0011	0.0010	84.697	14.984	0.110	0.110	0.100	HU466	800	47			13	Separated, resealed
												800	4			13	
126	0.4243	0.0751	0.0010			84.792	15.008	0.200	0.000	0.000		800	47			13	Separated, resealed.
												800	4			13	Cracked in furnace, oxidised.
127	0.4241	0.0753		0.0010		84.752	15.048	0.000	0.200	0.000	HU437	800	47			13	
132	0.4243	0.0749			0.0010	84.826	14.974	0.000	0.000	0.200	HU440	800	47			13	
133	0.4226	0.0748	0.0010	0.0010	0.0010	84.452	14.948	0.200	0.200	0.200	HU441	800	47			13	
594	1.6972	0.2996	0.0010	0.0013	0.0010	84.856	14.979	0.050	0.065	0.050	HU733	700	5			8	Duplicate of 124
595	0.4242	0.0749	0.0010			84.823	14.977	0.200	0.000	0.000	HU731	700	5			8	Duplicate of 126

Table A3. Ni-S charges for the 1000°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction		Melt		1000°C	Remarks
	Ni	S	Pt	Pd	Rh	Ni	S	Pt	Pd	Rh		°C	Days	°C	Days	Days	
5	0.4245	0.0750	0.0014			84.747	14.973	0.279	0.000	0.000	HU378	800	14	1200	10	42	
6	0.4245	0.0753		0.0013		84.714	15.027	0.000	0.259	0.000	HU379	800	14	1200	10	42	
7	0.4242	0.0750			0.0011	84.789	14.991	0.000	0.000	0.220	HU380	800	14	1200	10	42	
8	0.4226	0.0746	0.0010	0.0010	0.0010	84.486	14.914	0.200	0.200	0.200	HU381	800	14	1200	10	42	
25	1.6975	0.2996	0.0010	0.0010	0.0012	84.862	14.978	0.050	0.050	0.060	HU392	800	48			35	
26	0.8480	0.1499	0.0011	0.0013	0.0010	84.690	14.971	0.110	0.130	0.100	HU393	800	33			35	
31	0.4174	0.0739	0.0030	0.0034	0.0032	83.330	14.753	0.599	0.679	0.639	HU394	800	33			35	
32	0.4123	0.0728	0.0050	0.0050	0.0050	82.444	14.557	1.000	1.000	1.000	HU395	800	33			35	Quenched slower
48	0.4226	0.0749	0.0010	0.0016	0.0011	84.318	14.944	0.200	0.319	0.219	HU399	800	26			35	Duplicate of 8
95	0.4122	0.0730	0.0050	0.0050	0.0050	82.407	14.594	1.000	1.000	1.000	HU412	700	14	1100	5hrs	15	Duplicate of 32
96	0.3743	0.1248	0.0020			74.696	24.905	0.399	0.000	0.000	HU461	700	14	1100	5hrs	15	Separated, resealed
												700	3	1200	3	14	
106	0.3746	0.1248		0.0010		74.860	24.940	0.000	0.200	0.000	HU462	700	14	1100	5hrs	15	Separated, resealed
												700	3	1200	3	14	
107	0.3742	0.1249			0.0011	74.810	24.970	0.000	0.000	0.220	HU463	700	14	1100	5hrs	15	Separated, resealed
												700	3	1200	3	14	
108	0.3727	0.1243	0.0010	0.0010	0.0010	74.540	24.860	0.200	0.200	0.200	HU464	700	14	1100	5hrs	15	Separated, resealed
												700	3	1200	3	14	
109	0.3682	0.1232	0.0030	0.0030	0.0030	73.581	24.620	0.600	0.600	0.600	HU414	700	14	1100	5hrs	15	
110	0.3637	0.1213	0.0055	0.0050	0.0050	72.687	24.236	1.099	0.999	0.999	HU415	700	14	1100	5hrs	15	
111	0.7478	0.2495	0.0018	0.0010	0.0010	74.698	24.923	0.180	0.100	0.100	HU416	700	14	1100	5hrs	15	
118	1.4978	0.4992	0.0010	0.0016	0.0010	74.868	24.953	0.050	0.080	0.050		700	14	1100	5hrs	15	Separated, resealed.
												700	3	1100	3	14	Cracked during reaction, oxidised.

Table A4. Ni-S charges for the 900°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction		Melt		900°C	Remarks
	Ni	S	Pt	Pd	Rh	Ni	S	Pt	Pd	Rh		°C	Days	°C	Days	Days	
161	0.8474	0.1496	0.0010	0.0010	0.0011	84.732	14.959	0.100	0.100	0.110	HU753	800	43	1100	4	51	Separated, resealed
														1050	3	20	
162	1.6975	0.2995	0.0010	0.0010	0.0010	84.875	14.975	0.050	0.050	0.050		800	36	1100	4	51	Separated, resealed
														1050	3	20	Cracked in furnace, oxidised.
163	0.4241	0.0749	0.0011			84.803	14.977	0.220	0.000	0.000	HU426	800	43	1100	4	51	
164	0.4245	0.0752		0.0010		84.781	15.019	0.000	0.200	0.000	HU427	800	43	1100	4	51	
165	0.4241	0.0750			0.0014	84.735	14.985	0.000	0.000	0.280	HU428	800	43	1100	4	51	
166	0.4224	0.0746	0.0010	0.0010	0.0010	84.480	14.920	0.200	0.200	0.200	HU429	800	43	1100	4	51	
167	1.4978	0.4992	0.0011	0.0010	0.0012	74.879	24.956	0.055	0.050	0.060		800	36	1100	4	51	Separated, resealed
														1050	3	20	Cracked in furnace, oxidised.
168	0.7478	0.2492	0.0011	0.0010	0.0010	74.773	24.918	0.110	0.100	0.100		800	36	1100	4	51	Separated, resealed
														1050	3	20	Cracked in furnace, oxidised.
169	0.3729	0.1245	0.0010	0.0010	0.0014	74.461	24.860	0.200	0.200	0.280		800	43	1100	4	51	Separated, resealed
														1050	3	20	Cracked in furnace, oxidised.
173	0.3744	0.1250	0.0015			74.745	24.955	0.299	0.000	0.000	HU754	800	43	1100	4	51	Separated, resealed
														1050	3	20	
174	0.3742	0.1248		0.0010		74.840	24.960	0.000	0.200	0.000	HU433	800	43	1100	4	51	
175	0.3746	0.1249			0.0014	74.785	24.935	0.000	0.000	0.279	HU755	800	43	1100	4	51	Separated, resealed
														1050	3	20	
190	1.6975	0.2996	0.0010	0.0010	0.0010	84.871	14.979	0.050	0.050	0.050		800	4	1050	3	20	Duplicate of 162, oxidised in furnace.
191	0.8475	0.1496	0.0010	0.0011	0.0011	84.725	14.956	0.100	0.110	0.110		800	4	1050	3	20	Duplicate of 161, oxidised in furnace.

Table A5. Ni-S charges for the 800°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction		Melt		800°C	Remarks
	Ni	S	Pt	Pd	Rh	Ni	S	Pt	Pd	Rh		°C	Days	°C	Days	Days	
46	0.4241	0.0749		0.0010		84.820	14.980	0.000	0.200	0.000	HU481	800	56			52	
67	1.6975	0.2998	0.0011	0.0010	0.0010	84.858	14.987	0.055	0.050	0.050		800	30			52	Cracked in PRF, resealed, failed
68	0.8474	0.1500	0.0010	0.0012	0.0010	84.689	14.991	0.100	0.120	0.100		800	30			52	Cracked in PRF, resealed, failed

Table A6. Ni-S charges for the 700°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction		Melt		700°C	Remarks
	Ni	S	Pt	Pd	Rh	Ni	S	Pt	Pd	Rh		°C	Days	°C	Days	Days	
43	1.6975	0.2996	0.0010	0.0012	0.0010	84.862	14.978	0.050	0.060	0.050		800	56	1000	5hrs	23	Cracked in PRF, resealed, failed
44	0.8475	0.1496	0.0018	0.0012	0.0011	84.648	14.942	0.180	0.120	0.110		800	56	1000	5hrs	23	Cracked in PRF, resealed, failed
45	0.4246	0.0750	0.0010			84.818	14.982	0.200	0.000	0.000	HU470	800	56	1000	5hrs	23	
47	0.4246	0.0749			0.0012	84.801	14.959	0.000	0.000	0.240		800	56	1000	5hrs	23	Cracked in PRF, resealed, failed
59	0.4243	0.0750	0.0012			84.775	14.985	0.240	0.000	0.000	HU471	800	30	1000	5hrs	23	Duplicate of 45
60	0.4241	0.0751		0.0011		84.769	15.011	0.000	0.220	0.000	HU472	800	30	1000	5hrs	23	
61	0.4241	0.0749			0.0010	84.820	14.980	0.000	0.000	0.200	HU473	800	30	1000	5hrs	23	Duplicate of 47
62	0.4224	0.0748	0.0010	0.0010	0.0011	84.429	14.951	0.200	0.200	0.220	HU474	800	30	1000	5hrs	23	
79	0.4230	0.0745	0.0011	0.0010	0.0010	84.499	14.882	0.220	0.200	0.200	HU475	700	10	1000	5hrs	23	
94	1.6980	0.2998	0.0012	0.0010	0.0012	84.849	14.981	0.060	0.050	0.060	HU469	800	50	1000	5hrs	23	Duplicate of 43
187	0.4242	0.0750			0.0010	84.806	14.994	0.000	0.000	0.200	HU776	700	5	1050	1	12	Duplicate of 47, 61. Separated, resealed.
																18	
188	1.6975	0.2996	0.0010	0.0012	0.0010	84.862	14.978	0.050	0.060	0.050	HU777	700	5	1050	1	12	Duplicate of 43, 94. Separated, resealed.
																18	

Table A7. Cu-S charges for the 1200°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction		Melt		1200°C	Remarks
	Cu	S	Pt	Pd	Rh	Cu	S	Pt	Pd	Rh		°C	Days	°C	Days	Days	
137	1.7975	0.1997	0.0012	0.0011	0.0012	89.844	9.982	0.060	0.055	0.060		800	13			9	Cracked during reaction, oxidised.
138	0.8973	0.0997	0.0010	0.0010	0.0010	89.730	9.970	0.100	0.100	0.100	HU442	800	13			9	
139	0.4491	0.0499	0.0010			89.820	9.980	0.200	0.000	0.000	HU443	800	13			9	
140	0.4491	0.0499		0.0010		89.820	9.980	0.000	0.200	0.000	HU444	800	13			9	
141	0.4492	0.0499			0.0010	89.822	9.978	0.000	0.000	0.200	HU445	800	13			9	
147	0.4473	0.0497	0.0012	0.0010	0.0010	89.424	9.936	0.240	0.200	0.200	HU450	800	13			9	

Table A8. Cu-S charges for the 1100°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction		Melt		1100°C	Remarks
	Cu	S	Pt	Pd	Rh	Cu	S	Pt	Pd	Rh		°C	Days	°C	Days	Days	
128	0.4491	0.0500	0.0010			89.802	9.998	0.200	0.000	0.000		800	47			13	Separated, resealed.
												800	4			13	Cracked during reaction, oxidised.
129	0.4493	0.0499		0.0010		89.824	9.976	0.000	0.200	0.000	HU438	800	47			13	
130	0.4491	0.0499			0.0010	89.820	9.980	0.000	0.000	0.200	HU439	800	47			13	
131	0.4477	0.0499	0.0010	0.0011	0.0010	89.415	9.966	0.200	0.220	0.200	HU467	800	47			13	Separated, resealed
												800	4			13	
134	1.7972	0.1997	0.0012	0.0010	0.0011	89.851	9.984	0.060	0.050	0.055		800	47			13	Cracked during reaction.
135	0.8977	0.0997	0.0010	0.0011	0.0010	89.725	9.965	0.100	0.110	0.100	HU468	800	47			13	Separated, resealed
												800	4			13	
211	1.7979	0.1997	0.0015	0.0013	0.0010	89.832	9.978	0.075	0.065	0.050		800	4			13	Duplicate of 134, separated, resealed
																8	Separated again.

Table A9. Cu-S charges for the 1000°C isothermal section

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction		Melt		1000°C	Remarks
	Cu	S	Pt	Pd	Rh	Cu	S	Pt	Pd	Rh		°C	Days	°C	Days	Days	
9	0.4494	0.0498	0.0018			89.701	9.940	0.359	0.000	0.000	HU382	800	14	1200	10	42	
10	0.4494	0.0498		0.0016		89.736	9.944	0.000	0.319	0.000	HU383	800	14	1200	10	42	
11	0.4492	0.0499			0.0015	89.732	9.968	0.000	0.000	0.300	HU384	800	14	1200	10	42	
12	0.4473	0.0497	0.0011	0.0015	0.0010	89.353	9.928	0.220	0.300	0.200	HU385	800	14	1200	10	42	
17	0.3888	0.1099	0.0011	0.0013	0.0011	77.419	21.884	0.219	0.259	0.219		800	59				Failed in PRF
18	1.7975	0.1997	0.0010	0.0011	0.0011	89.857	9.983	0.050	0.055	0.055	HU386	800	59			35	
19	0.8973	0.0995	0.0010	0.0010	0.0015	89.703	9.947	0.100	0.100	0.150	HU387	800	59			35	
20	0.3892	0.1098	0.0012			77.809	21.951	0.240	0.000	0.000	HU388	800	12			40	Cracked during quenching
21	0.3899	0.1098		0.0010		77.871	21.929	0.000	0.200	0.000	HU389	800	12			40	Cracked during quenching
22	0.3898	0.1098			0.0010	77.867	21.934	0.000	0.000	0.200	HU390	800	12			40	Cracked during quenching
23	0.7777	0.2193	0.0012	0.0012	0.0010	77.739	21.921	0.120	0.120	0.100		800	18				Failed in PRF
24	1.5580	0.4398	0.0010	0.0014	0.0015	77.834	21.971	0.050	0.070	0.075	HU391	800	48			35	
33	0.4460	0.0494	0.0030	0.0030	0.0030	88.422	9.794	0.595	0.595	0.595	HU396	800	40			35	
34	0.4378	0.0485	0.0050	0.0049	0.0050	87.350	9.677	0.998	0.978	0.998		800	40				Failed in PRF
35	0.3829	0.1080	0.0030	0.0030	0.0034	76.534	21.587	0.600	0.600	0.680	HU397	800	40			35	
36	0.3785	0.1065	0.0052	0.0051	0.0051	75.639	21.283	1.039	1.019	1.019	HU398	800	40			35	
54	0.7777	0.2193	0.0010	0.0011	0.0014	77.731	21.919	0.100	0.110	0.140	HU400	800	26			35	Duplicate of 23
91	0.4365	0.0487	0.0050	0.0050	0.0053	87.213	9.730	0.999	0.999	1.059		700	14	1100	5hrs	15	Duplicate of 34, failed in furnace.
92	0.3880	0.1093	0.0010	0.0010	0.0015	77.476	21.825	0.200	0.200	0.300	HU411	700	14	1100	5hrs	15	Duplicate of 17
102	0.7777	0.2193	0.0010	0.0010	0.0010	77.770	21.930	0.100	0.100	0.100	HU413	700	14	1100	5hrs	15	Duplicate of 23, 54
183	0.4492	0.0499		0.0010		89.822	9.978	0.000	0.200	0.000	HU417	700	14	1100	5hrs	15	Duplicate of 10
184	0.3898	0.1100	0.0017			77.727	21.934	0.339	0.000	0.000	HU418	700	14	1100	5hrs	15	Duplicate of 20
185	0.3895	0.1098		0.0010		77.853	21.947	0.000	0.200	0.000	HU419	700	14	1100	5hrs	15	Duplicate of 21
186	0.3892	0.1098			0.0010	77.840	21.960	0.000	0.000	0.200	HU420	700	14	1100	5hrs	15	Duplicate of 22
210	0.4367	0.0490	0.0050	0.0055	0.0050	87.131	9.777	0.998	1.097	0.998	HU365	700	3	1200	3	14	Duplicate of 34, 91

Table A10. Cu-S charges for the 900°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction		Melt		900°C	Remarks
	Cu	S	Pt	Pd	Rh	Cu	S	Pt	Pd	Rh		°C	Days	°C	Days	Days	
152	1.7973	0.1997	0.0010	0.0010	0.0010	89.865	9.985	0.050	0.050	0.050		800	35	1100	4	51	Separated, resealed
														1050	3	20	Oxidised in furnace.
153	0.8973	0.0999	0.0010	0.0010	0.0010	89.712	9.988	0.100	0.100	0.100		800	43	1100	4	51	Separated, resealed
														1050	3	20	Separated again.
154	0.4493	0.0500	0.0010			89.806	9.994	0.200	0.000	0.000		800	43	1100	4	51	Separated, resealed
														1050	3	20	Oxidised in furnace.
155	0.4491	0.0499		0.0010		89.820	9.980	0.000	0.200	0.000	HU421	800	43	1100	4	51	
156	0.4494	0.0502			0.0015	89.683	10.018	0.000	0.000	0.299	HU422	800	43	1100	4	51	
157	0.4474	0.0497	0.0012	0.0011	0.0010	89.408	9.932	0.240	0.220	0.200	HU423	800	43	1100	4	51	
159	0.7777	0.2193	0.0010	0.0010	0.0010	77.770	21.930	0.100	0.100	0.100	HU424	800	43	1100	4	51	Cracked in PRF, resealed
160	0.3878	0.1093	0.0011	0.0010	0.0012	77.498	21.843	0.220	0.200	0.240	HU425	800	43	1100	4	51	
170	0.3892	0.1098	0.0013			77.793	21.947	0.260	0.000	0.000	HU430	800	43	1100	4	51	
171	0.3891	0.1098		0.0010		77.836	21.964	0.000	0.200	0.000	HU431	800	43	1100	4	51	
172	0.3894	0.1098			0.0010	77.849	21.951	0.000	0.000	0.200	HU432	800	43	1100	4	51	
179	1.5579	0.4397	0.0012	0.0010	0.0010	77.864	21.976	0.060	0.050	0.050		800	35	1050	3	20	Cracked in PRF, resealed, failed in furnace.

Table A11. Cu-S charges for the 800°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction		Melt		800°C	Remarks
	Cu	S	Pt	Pd	Rh	Cu	S	Pt	Pd	Rh		°C	Days	°C	Days	Days	
38	0.4494	0.0499	0.0010			89.826	9.974	0.200	0.000	0.000	HU483	800	70			52	
39	0.4493	0.0499		0.0010		89.824	9.976	0.000	0.200	0.000	HU484	800	56			52	
40	0.4490	0.0500			0.0013	89.746	9.994	0.000	0.000	0.260	HU485	800	56			52	
42	0.8973	0.0997	0.0015	0.0011	0.0010	89.676	9.964	0.150	0.110	0.100	HU482	800	56			52	
71	0.4477	0.0497	0.0013	0.0010	0.0012	89.379	9.922	0.260	0.200	0.240		800	30			52	Cracked, oxidised.
78	1.7973	0.1999	0.0010	0.0010	0.0010	89.856	9.994	0.050	0.050	0.050		700	51			52	Cracked, oxidised.

Table A12. Cu-S charges for the 700°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction		Melt		700°C	Remarks
	Cu	S	Pt	Pd	Rh	Cu	S	Pt	Pd	Rh		°C	Days	°C	Days	Days	
41	0.4473	0.0500	0.0010	0.0010	0.0012	89.371	9.990	0.200	0.200	0.240		800	56	1000	5hrs	23	Cracked, oxidised.
49	1.7973	0.1999	0.0012	0.0011	0.0010	89.843	9.993	0.060	0.055	0.050		800	26				Failed in PRF
65	0.4493	0.0499	0.0014			89.752	9.968	0.280	0.000	0.000	HU779	800	30	1000	5hrs	23	Separated
												700	5	1050	1	12	
69	0.4493	0.0499		0.0010		89.824	9.976	0.000	0.200	0.000	HU477	800	30	1000	5hrs	23	
70	0.4491	0.0499			0.0011	89.802	9.978	0.000	0.000	0.220	HU478	800	30	1000	5hrs	23	
77	0.8973	0.0997	0.0010	0.0012	0.0010	89.712	9.968	0.100	0.120	0.100	HU476	700	20	1000	5hrs	23	
100	1.7975	0.1997	0.0010	0.0013	0.0011	89.848	9.982	0.050	0.065	0.055		800	50	1000	5hrs	23	Duplicate of 49, failed

Table A13. Fe-S charges for the 1200°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction				Melt		1200°C	Remarks
	Fe	S	Pt	Pd	Rh	Fe	S	Pt	Pd	Rh		°C	Days	°C	Days	°C	Days	Days	
212	0.3927	0.0999	0.0011			79.542	20.235	0.223	0.000	0.000	HU825	800	41	700	149			2	Cracked in PRF, resealed, cracked and resealed 2nd time.
213	0.3933	0.0986		0.0013		79.745	19.992	0.000	0.264	0.000	HU826	800	41	700	149			2	Cracked in PRF, resealed
214	0.3919	0.0987			0.0010	79.719	20.077	0.000	0.000	0.203	HU827	800	41	700	149			2	Cracked in PRF, resealed
215	0.3219	0.1733	0.0011			64.860	34.918	0.222	0.000	0.000		800	41	700	149			2	Cracked in PRF, resealed, cracked and resealed 2nd time, oxidised at 1200°C.
216	0.3238	0.1744		0.0013		64.825	34.915	0.000	0.260	0.000		800	41	700	149			2	Cracked in PRF, resealed, oxidised at 1200°C
217	0.3212	0.1729			0.0012	64.850	34.908	0.000	0.000	0.242		800	41	700	149			2	Cracked in PRF, resealed, cracked and resealed 2nd time, oxidised at 1200°C.

Table A14. Fe-S charges for the 1100°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction				Melt		1100°C	Remarks
	Fe	S	Pt	Pd	Rh	Fe	S	Pt	Pd	Rh		°C	Days	°C	Days	°C	Days	Days	
218	0.3914	0.0982	0.0012			79.747	20.008	0.244	0.000	0.000	HU734	700	149					8	Uncertain of equilibrium conditions.
219	0.3921	0.0980		0.0012		79.809	19.947	0.000	0.244	0.000	HU735	700	149					8	
220	0.3906	0.0979			0.0010	79.796	20.000	0.000	0.000	0.204	HU736	700	149					8	Uncertain of equilibrium conditions.
221	0.3207	0.1727	0.0010			64.867	34.931	0.202	0.000	0.000	HU737	700	149					8	Uncertain of equilibrium conditions.
222	0.3212	0.1730		0.0010		64.863	34.935	0.000	0.202	0.000	HU738	700	149					8	Resealed after prereaction.
223	0.3198	0.1724			0.0010	64.842	34.955	0.000	0.000	0.203	HU739	700	149					8	Cracked during prereaction.

Table A15. Fe-S charges for the 1000°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction				Melt		1000°C	Remarks
	Fe	S	Pt	Pd	Rh	Fe	S	Pt	Pd	Rh		°C	Days	°C	Days	°C	Days	Days	
1	0.3993	0.0999	0.0012			79.796	19.964	0.240	0.000	0.000		800	15			1200	10	2	Completely oxidised in furnace.
2	0.3999	0.0999		0.0013		79.804	19.936	0.000	0.259	0.000		800	15			1200	10	2	Completely oxidised in furnace.
3	0.3994	0.1002			0.0010	79.784	20.016	0.000	0.000	0.200		800	15			1200	10	2	Completely oxidised in furnace.
4	0.3985	0.1005	0.0010	0.0014	0.0014	79.256	19.988	0.199	0.278	0.278		800	15			1200	10	2	Completely oxidised in furnace.
13	0.3242	0.1746	0.0010			64.866	34.934	0.200	0.000	0.000		800	89						Failed in PRF
14	0.3242	0.1748		0.0010		64.840	34.960	0.000	0.200	0.000		800	89						Failed in PRF
15	0.3246	0.1748			0.0010	64.868	34.932	0.000	0.000	0.200		800	89						Failed in PRF
16	0.3232	0.1745	0.0012	0.0013	0.0013	64.447	34.796	0.239	0.259	0.259		800	89						Failed in PRF
27	0.3946	0.0984	0.0032	0.0028	0.0031	78.590	19.598	0.637	0.558	0.617		800	32						Failed in PRF
28	0.3880	0.0970	0.0050	0.0050	0.0050	77.600	19.400	1.000	1.000	1.000		800	32						Failed in PRF
29	0.3199	0.1719	0.0030	0.0030	0.0029	63.891	34.332	0.599	0.599	0.579		800	32						Failed in PRF
30	0.3153	0.1698	0.0050	0.0050	0.0050	63.047	33.953	1.000	1.000	1.000		800	32						Failed in PRF
37	1.2980	0.6999	0.0015	0.0017	0.0015	64.816	34.950	0.075	0.085	0.075		800	21						Failed in PRF
64	0.7976	0.1995	0.0010	0.0010	0.0010	79.752	19.948	0.100	0.100	0.100		800	56						Failed in PRF
66	1.5976	0.3994	0.0010	0.0010	0.0010	79.880	19.970	0.050	0.050	0.050		800	56						Failed in PRF
98	0.7977	0.1994	0.0010	0.0010	0.0010	79.762	19.938	0.100	0.100	0.100		800	41						Duplicate of 64, failed in PRF
104	0.6442	0.3464	0.0010	0.0011	0.0015	64.796	34.842	0.101	0.111	0.151		800							Exploded in PRF
105	0.3958	0.0990	0.0010			79.831	19.968	0.202	0.000	0.000		800	41						Duplicate of 1, failed in PRF
112	0.3979	0.0995		0.0011		79.819	19.960	0.000	0.221	0.000	HU843	800	41	700	149			15	Duplicate of 2, cracked in PRF, resealed twice
113	0.3975	0.0995			0.0010	79.819	19.980	0.000	0.000	0.201	HU844	800	41	700	149			15	Duplicate of 3, cracked in PRF, resealed
114	0.3948	0.0987	0.0011	0.0010	0.0010	79.501	19.875	0.222	0.201	0.201	HU845	800	41	700	149			15	Duplicate of 4, cracked in PRF, resealed
115	0.3230	0.1739	0.0010			64.872	34.927	0.201	0.000	0.000	HU846	800	41	700	149			15	Duplicate of 13, cracked in PRF, resealed twice
116	0.3216	0.1732		0.0011		64.852	34.926	0.000	0.222	0.000	HU847	800	41	700	149			15	Duplicate of 14, cracked in PRF, resealed
117	0.3235	0.1747			0.0010	64.804	34.996	0.000	0.000	0.200	HU848	800	41	700	149			15	Duplicate of 15, cracked in PRF, resealed
119	0.3929	0.0982	0.0030	0.0031	0.0030	78.549	19.632	0.600	0.620	0.600	HU849	800	41	700	149			15	Duplicate of 27, cracked in PRF, resealed
120	0.3885	0.0971	0.0050	0.0050	0.0054	77.545	19.381	0.998	0.998	1.078	HU850	800	41	700	149			15	Duplicate of 28, cracked in PRF, resealed
121	0.3176	0.1710	0.0030	0.0035	0.0030	63.762	34.330	0.602	0.703	0.602		800	41						Duplicate of 29, failed in PRF
122	0.3157	0.1700	0.0050	0.0051	0.0050	63.039	33.946	0.998	1.018	0.998	HU851	800	41	700	149			15	Duplicate of 30, cracked in PRF, resealed
123	0.3232	0.1741	0.0010	0.0010	0.0010	64.601	34.799	0.200	0.200	0.200	HU852	800	41	700	149			15	Duplicate of 16, cracked in PRF, resealed twice
150	1.5918	0.3980	0.0010	0.0014	0.0010	79.862	19.968	0.050	0.070	0.050		800							Duplicate of 66, exploded in PRF
151	1.2940	0.6968	0.0010	0.0012	0.0011	64.891	34.943	0.050	0.060	0.055		800							Duplicate of 37, exploded in PRF

Table A16. Fe-S charges for the 900°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction				Melt		900°C	Remarks
	Fe	S	Pt	Pd	Rh	Fe	S	Pt	Pd	Rh		°C	Days	°C	Days	°C	Days	Days	
176	0.3923	0.0980	0.0009			79.866	19.951	0.183	0.000	0.000	HU434	800	43			1100	4	51	
177	0.3992	0.0981		0.0013		80.064	19.675	0.000	0.261	0.000	HU435	800	43			1100	4	51	
178	0.3937	0.0986			0.0011	79.793	19.984	0.000	0.000	0.223	HU436	800	43			1100	4	51	
180	0.7880	0.1970	0.0014	0.0010	0.0010	79.725	19.931	0.142	0.101	0.101	HU756	800	34			1050	3	20	Cracked in PRF, resealed, separated, not equilibrium.
181	0.3909	0.0977	0.0012	0.0011	0.0010	79.467	19.862	0.244	0.224	0.203		800	34			1050	3	20	Cracked in PRF, resealed, oxidised in furnace.
182	1.5758	0.3940	0.0011	0.0010	0.0010	79.872	19.971	0.056	0.051	0.051		800	6			1050	3	20	Cracked in PRF, resealed, oxidised in furnace.

Table A17. Fe-S charges for the 800°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction				Melt		800°C	Remarks
	Fe	S	Pt	Pd	Rh	Fe	S	Pt	Pd	Rh		°C	Days	°C	Days	°C	Days	Days	
85	0.3992	0.0996	0.0010			79.872	19.928	0.200	0.000	0.000	HU785	800	93					12	Cracked in PRF, resealed
86	0.3991	0.0996		0.0010		79.868	19.932	0.000	0.200	0.000	HU784	800	93					12	Cracked in PRF, resealed
87	0.3993	0.1000			0.0012	79.780	19.980	0.000	0.000	0.240		800	93						Failed in PRF
88	0.3936	0.0988	0.0010	0.0010	0.0013	79.403	19.931	0.202	0.202	0.262	HU783	800	93					12	Cracked in PRF, resealed
97	0.7686	0.1971	0.0010	0.0010	0.0011	79.753	19.933	0.101	0.101	0.111	HU786	800	62					12	Cracked in PRF, resealed
99	1.5876	0.3969	0.0010	0.0013	0.0010	79.867	19.967	0.050	0.065	0.050	HU782	800	62					12	Failed in PRF
149	1.5893	0.3977	0.0010	0.0010	0.0010	79.864	19.985	0.050	0.050	0.050		800							Duplicate of 99, exploded in PRF

Table A18. Fe-S charges for the 700°C isothermal section.

Charge nr	Weight measured (g)					Weight %					Exp	Pre-reaction				Melt		700°C	Remarks
	Fe	S	Pt	Pd	Rh	Fe	S	Pt	Pd	Rh		°C	Days	°C	Days	°C	Days	Days	
55	0.3992	0.0998	0.0012			79.808	19.952	0.240	0.000	0.000		800	56						Failed in PRF
56	0.3992	0.0998		0.0010		79.840	19.960	0.000	0.200	0.000		800	56						Failed in PRF
57	0.3992	0.0998			0.0010	79.840	19.960	0.000	0.000	0.200		800	56						Failed in PRF
58	0.3976	0.0994	0.0010	0.0015	0.0010	79.441	19.860	0.200	0.300	0.200		800	56						Failed in PRF
82	0.3992	0.0998	0.0015			79.760	19.940	0.300	0.000	0.000		800	93	700	5	1050	1	12	Duplicate of 55, cracked in PRF, resealed, oxidised
83	0.3995	0.1000		0.0010		79.820	19.980	0.000	0.200	0.000		800	93						Duplicate of 56, failed
84	0.3992	0.0998			0.0010	79.840	19.960	0.000	0.000	0.200		800	93	700	5	1050	1	12	Duplicate of 57, cracked in PRF, resealed, oxidised
89	0.3941	0.0985	0.0010	0.0014	0.0010	79.456	19.659	0.202	0.282	0.202		800	93						Duplicate of 58, failed in PRF
93	0.7916	0.1980	0.0010	0.0011	0.0010	79.742	19.946	0.101	0.111	0.101		800	63						Failed in PRF
103	1.5934	0.3984	0.0010	0.0013	0.0010	79.866	19.969	0.050	0.065	0.050		800	31						Failed in PRF
148	1.5888	0.3972	0.0010	0.0013	0.0010	79.867	19.967	0.050	0.065	0.050		800							Duplicate of 103, exploded in PRF

Abstract

Partitioning of platinum-group elements between metal and sulphide melt in the Cu-S and Ni-S systems.

By

Henriëtte Ueckermann

Study leader: Prof. R. K. W. Merkle

Degree: M. Sc. Applied Mineralogy

The partitioning behaviour of the three platinum-group elements (PGE), Rh, Pd and Pt, was investigated at trace concentrations between phases in the systems Cu-S and Ni-S at low S contents. Additional exploratory investigations of partitioning in the Fe-S system were also performed. Experiments were equilibrated in quartz tubes at temperatures between 1200°C and 700°C, and were analysed by Electron Probe Micro Analyser for the major elements and Particle Induced X-ray Emission for the trace elements. Quantitative data on the partitioning of PGE at temperatures relevant to the formation and development of PGE deposits are of great importance in the exploration, ore beneficiation, and metallurgy of PGE.

Both Pt and Rh are compatible with nickel as opposed to sulphide melt at all temperatures investigated. D_{Rh} increases from 1.6 at 1100°C to 9.9 at 700°C, and similarly D_{Pt} from 4 to 200. Pd is concentrated in the melt, with D_{Pd} similarly increasing from 0.5 to 0.9. All three become more compatible with nickel as the temperature decreases. As the sulphur content of the melt increases at lower temperatures, other researchers (e.g. Li *et al.*, 1996; Fleet *et al.*, 1999) have suggested that partition coefficients are more dependent on the S content in the melt than on temperature itself, but in this investigation the two factors could not be discriminated.

Rh, Pd and Pt were all concentrated in the Cu-rich melt that co-exists with S-rich melt at 1200°C, with $D_{Rh} > 10$, $D_{Pd} \sim 7.5$, and $D_{Pt} > 3$. All three PGE were concentrated in the sulphide melt that co-exists with digenite at 1000°C, with D_{Rh} varying from 4 to 62, D_{Pd} from 2.9 to 4.8, and D_{Pt} from 12.7 to 23.6. All three platinum-group elements also prefer the copper as opposed to the digenite at 1000°C, with $D_{Rh} > 15$ at 1000°C and ~45 at 800°C, D_{Pd} varying from 23 to 675 – differing between instruments - and $D_{Pt} > 13$.

Rh and Pt preferably partition into iron that co-exists with sulphide melt at 1200°C, 1100°C and 1000°C. $D_{Rh} > 2$ and $D_{Pt} > 1.1$, and probably much larger. D_{Pd} changes from slightly incompatible at 1200°C (0.98) to compatible at 1000°C (>1.2). All three PGE partition into sulphide melt that co-exists with pyrrhotite at 1100°C, with $D_{Rh} > 3.7$, $D_{Pd} > 10.5$, and $D_{Pt} > 3.8$. At 900°C all three PGE partition into iron as opposed to troilite, with $D_{Rh} > 2.1$, $D_{Pd} \sim 1.2$, and $D_{Pt} > 1.6$.

Uittreksel

Skeiding van platinum-groep elemente tussen metaal en sulfied smeltsels in die Cu-S and Ni-S sisteme.

Deur

Henriëtte Ueckermann

Studie leier: Prof. R. K. W. Merkle

Graad: M. Sc. Applied Mineralogy

Die verdelingsgedrag van die drie platinum-groep elemente (PGE), Rh, Pd en Pt, in spoor hoeveelhede, is by lae S inhoude in die Cu-S en Ni-S stelsels ondersoek. Bykomende eksploratoriese ondersoeke van verdeling is ook in die Fe-S stelsel gedoen. Eksperimente is ge-ekwilibreer in kwarts glasbuisies by temperature tussen 1200°C en 700°C. Hoofelemente is bepaal deur wyse van elektron mikrosonde analises en spoorelemente deur Partikel geinduseerde X-straal emissie analises. Kwantitatiewe data van die skeidingsgedrag van PGE by temperature relefant tot die vorming en ontwikkeling van PGE afsettings is van groot belang vir die eksplorasie, benefisiering en metallurgie van PGE.

Beide Rh en Pt verkies nikkel teenoor die sulfied smeltsel by al die temperature wat ondersoek is. D_{Rh} neem toe van 1.6 by 1100°C tot 9.9 by 700°C, en soortgelyk D_{Pt} van 4 tot 200. Pd konsentreer in die smeltsel, met D_{Pd} wat soortgelyk toeneem van 0.5 tot 0.9. Al drie PGE konsentreer tot 'n hoër mate in die nikkel by laer temperature. Aangesien die S inhoud van die smeltsel toeneem by laer temperature, is daar deur ander navorsers (bv. Li *et al.*, 1996; Fleet *et al.*, 1999) voorgestel dat verdelingskoëffisiente eerder meer afhanklik is van die S inhoud van die smeltsel as die temperatuur, maar in die huidige studie kan daar nie tussen hierdie twee faktore onderskei word nie.

Rh, Pd en Pt is almal gekonsentreer in die Cu-ryke smeltsel wat saam met die S-ryke smeltsel voorkom by 1200°C, met $D_{Rh} > 10$, $D_{Pd} \sim 7.5$, en $D_{Pt} > 3$. Al drie PGE is in die sulfied smeltsel wat saam met digeniet by 1000°C voorkom gekonsentreer, met D_{Rh} wisselend van 4 tot 62, D_{Pd} van 2.9 tot 4.8, en D_{Pt} van 12.7 tot 23.6. Al drie PGE verkies ook koper bo digeniet by 1000°C, met $D_{Rh} > 15$ by 1000°C en ~45 by 800°C, D_{Pd} wisselend van 23 tot 675 – en verskillend van instrument tot instrument – en $D_{Pt} >13$.

Rh and Pt verdeel eerder in die yster wat saam met sulfied smeltsel voorkom by 1200°C, 1100°C and 1000°C. D_{Rh} is > 2 en $D_{Pt} > 1.1$, en waarskynlik baie groter. Pd verander van effens gekonsentreer in die smeltsel by 1200°C (0.98) tot meer gekonsentreerd in die yster by 1000°C (>1.2). Al drie PGE verkies die sulfied smeltsel bo pyrrhotiet by 1100°C, met $D_{Rh} > 3.7$, $D_{Pd} > 10.5$, en $D_{Pt} > 3.8$. By 900°C verkies al drie PGE yster teenoor troiliet, met $D_{Rh} > 2.1$, D_{Pd} ongeveer 1.2, en $D_{Pt} > 1.6$.