Al-Ir Compounds and the Problem of Light Element-Heavy Element Matrix Corrections in EPMA: Application of PENEPMA Monte Carlo Modeling

John Fournelle*, Chuan Zhang** and Y. Austin Chang**

* Department of Geology and Geophysics, University of Wisconsin, Madison, WI 53706
** Department of Material Science and Engineering, University of Wisconsin, Madison WI 53706

Little has been published regarding difficulties in correcting matrix effects in materials where there was a wide disparity in atomic number (Z) between 2 elements in a compound. Here we discuss difficulties in compounds of Al-Ir (Z of 13-77). The first indication of a problem appeared as a low total (e.g., 96 wt%). Missing element? (nothing obvious) Oxide coating? (no) Charging sample? (no). John Armstrong [1] and Paul Carpenter [2] have mentioned a similar issue at CalTech years ago, for a Si-Ir sample where, using pure Si and pure Ir standards, significantly different results were possible depending upon which correction scheme was used. Their solution was for the researchers to synthesize an intermediate compound that was then used as a standard – then the matrix corrections were less extreme. This approach is a good one, and can "save your bacon" where it is feasible, but is not always possible. Additional considerations include inaccuracies with the MACs: in the case here, there are significant differences (26%) for the MACs for Al Ka in Ir: from 2351 (Heinrich 1966) to the "modern" 1738 (FFAST: Chandler 2005). MACs for Ir Ma in Al are quite similar (<4% difference). Another complication could be determination of the mean atomic number particularly where the backscatter correction is explicitly used [3].

Consider the dark BSE contrast phase (1130°C), with the highest amount of Al (Figure 1). Tables 1-3 shows the results of running 10 different matrix corrections with 3 different MACs (here, in Probe for Windows), with ~15% range for Al and ~5% for Ir (wt% values). One is left in a quandary as to which set of values to trust: there are generally 2 or 3 groupings of data, which differ by ~5 atomic percent. We ran simple (bulk geometry) Monte Carlo simulations with PENEPMA [4] for several putative compositions for the dark phase, to find which closest reproduced the observed K-ratios. We could not match both Al and Ir k-ratios for the exact same compound, and found a "best fit" as Ir 51.5, Al 48.5 (Figure 2). We did the same for the bright phase, with a best fit of Ir 93, Al 7. (Figure 3). These values match the older published phase diagram [5], while contradicting [6] for the bright phase. Hutchinson, who was involved in that study's EPMA 2 decades ago, said they used SANDIATASK which had a modified Phi Rho Z from Bastin and MACs "from Jane Frazer @ Scripps with modifications" [7]. The values shown in Table 1 for the 2 Bastin calculations (with Henke MACs) match the values suggested by PENEPMA.

References

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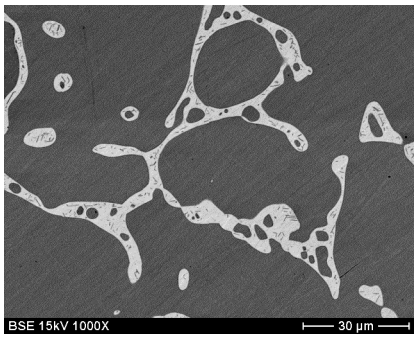

TABLE 1	MACs: Henke (1985)				Al ka by Ir: 2057
Al wt%	Ir wt%	Total wt%	Al at%	Ir at%	
12.19	84.25	96.44	50.7	49.3	Armstrong/Love Scott (default)
9.60	89.02	98.62	43.4	56.6	Conventional Philibert/Duncumb-Reed
11.07	87.06	98.13	47.5	52.5	Heinrich/Duncumb-Reed
11.05	84.43	95.47	48.2	51.8	Love-Scott I
11.00	84.88	95.89	48.0	52.0	Love-Scott II
9.52	86.54	96.05	43.9	56.1	Packwood Phi(pz) (EPQ-91)
11.65	88.96	100.62	48.3	51.7	Bastin (original) Phi(pz)
11.63	87.17	98.80	48.7	51.3	Bastin PROZA Phi(pz) (EPQ-91)
11.02	86.27	97.28	47.6	52.4	Pouchou and Pichoir - Full
10.86	85.88	96.75	47.4	52.6	Pouchou and Pichoir - Simplified

Fig 1: BSE image of alloy Ir-46.20Al annealed at 1130°C for more than 1000 hours. The bright phase is fcc-(Ir) and the dark one is B2-AlIr.

TABLE 2	MACs: Heinrich (1966)+	Al ka by Ir 2351		
Al wt%	Ir wt%	Total wt%	Al at%	Ir at%
13.02	84.28	97.31	52.4	47.6
10.19	89.44	99.63	44.8	55.2
11.73	87.35	99.08	48.9	51.1
11.74	84.57	96.31	49.7	50.3
11.69	85.10	96.79	49.5	50.5
10.23	86.73	96.96	45.7	54.3
12.47	89.20	101.67	49.9	50,1
12.43	87.53	99.96	50.3	49.7
11.77	86.50	98.26	49.2	50.8
11.59	86.08	97.67	49.0	51.0

TABLE 3	MACs: FFAST		Al ka by Ir: 1738	
Al wt%	Ir wt%	Total wt%	Al at%	Ir at%
11.42	84.72	96.14	49.0	51.0
9.09	88.93	98.02	42.1	57.9
10.50	87.12	97.62	46.2	53.8
10.43	84.62	95.05	46.8	53.2
10.40	84.99	95.39	46.6	53.4
8.85	86.75	95.60	42.1	57.9
10.91	89.17	100.08	46.6	53.4
10.88	87.17	98.05	47.1	52.9
10.34	86.45	96.79	46.0	54.0
10.22	86.07	96.29	45.8	54.2

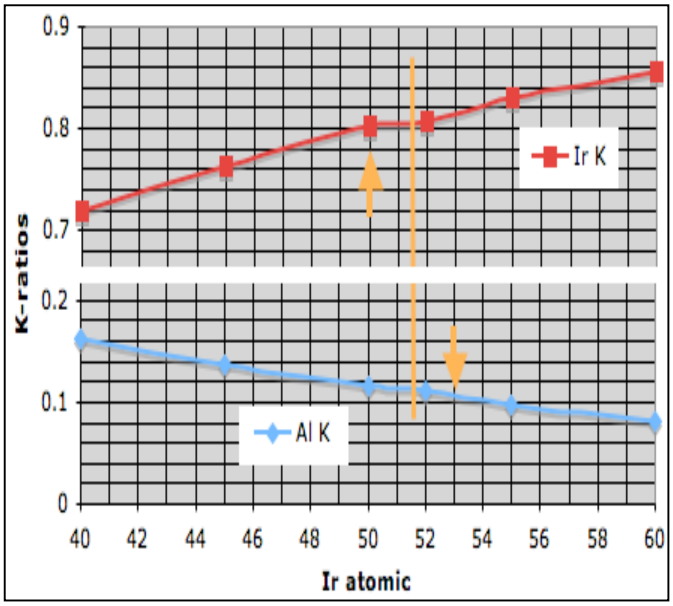

Fig. 2. Simulations of 6 intermediate Al-Ir compounds with PENEPMA, to match observed K-ratios for dark phase

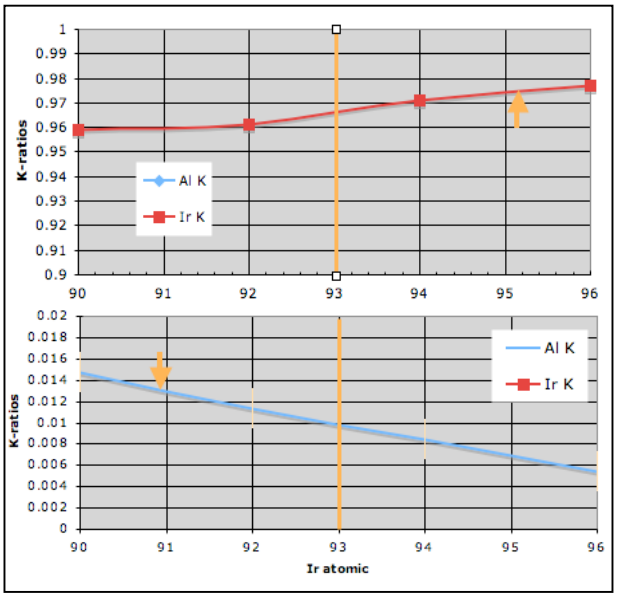

Fig. 3. Simulations of 4 intermediate low Al compounds with PENEPMA, to match observed K-ratios for bright phase